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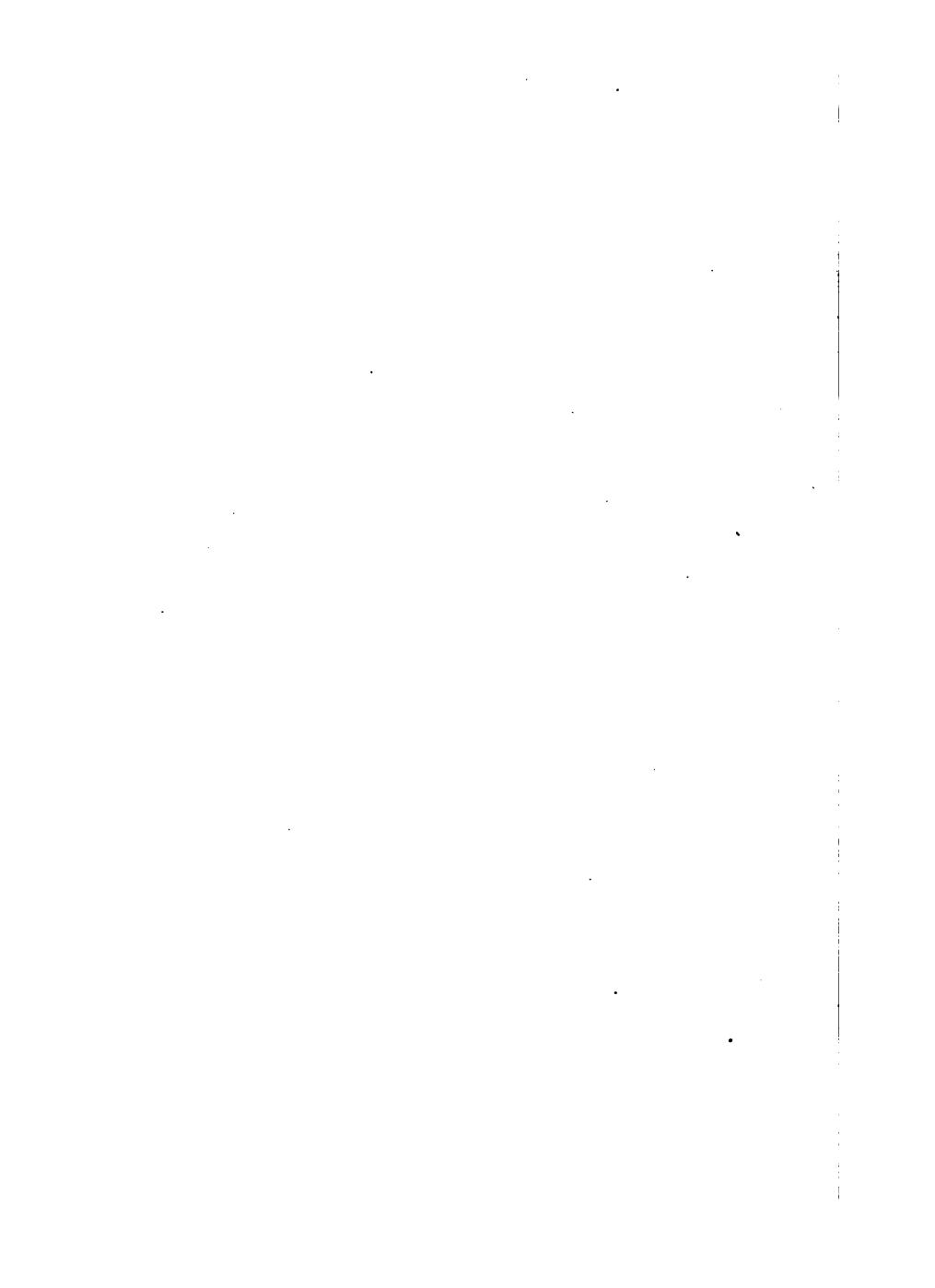


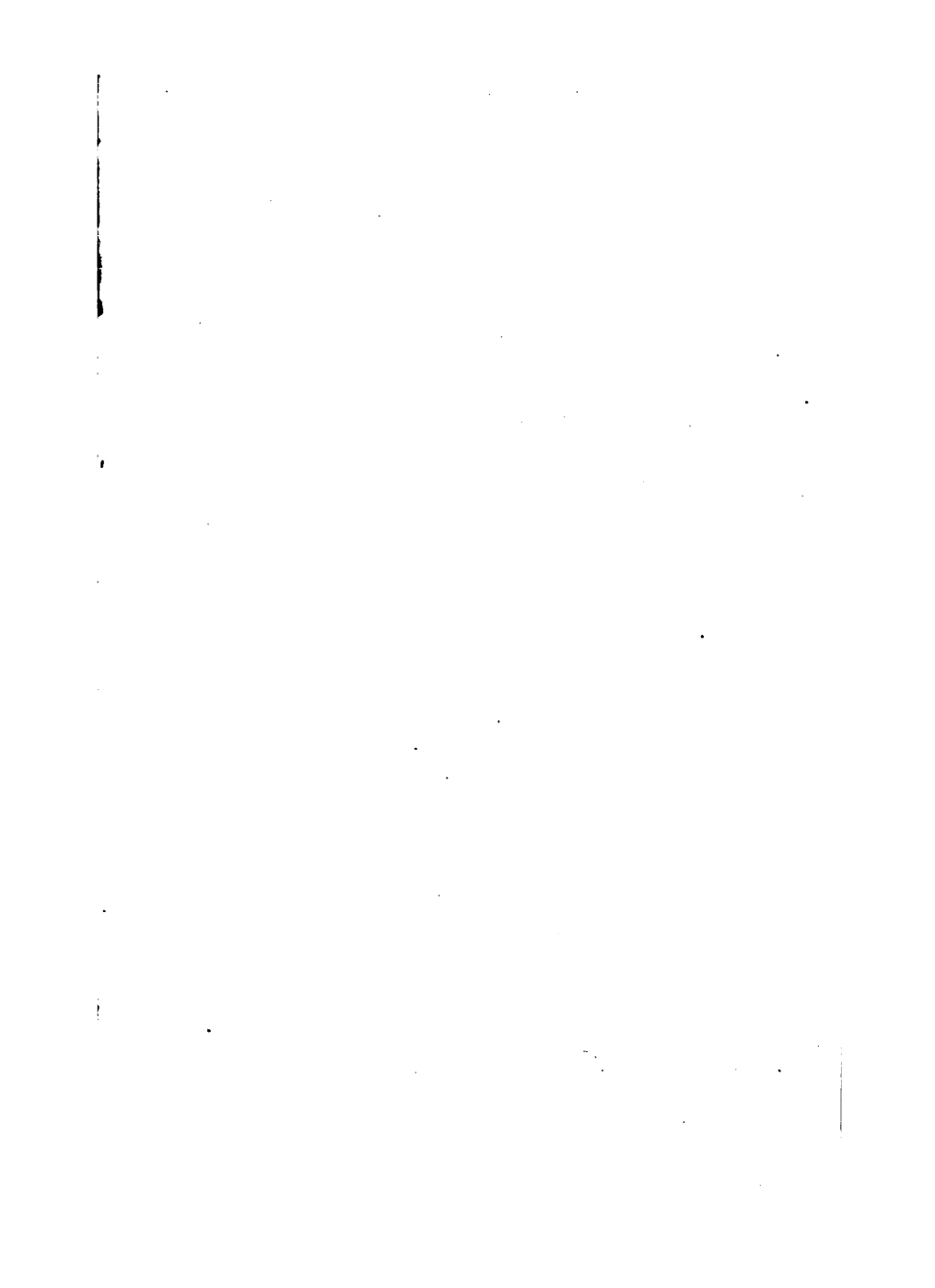
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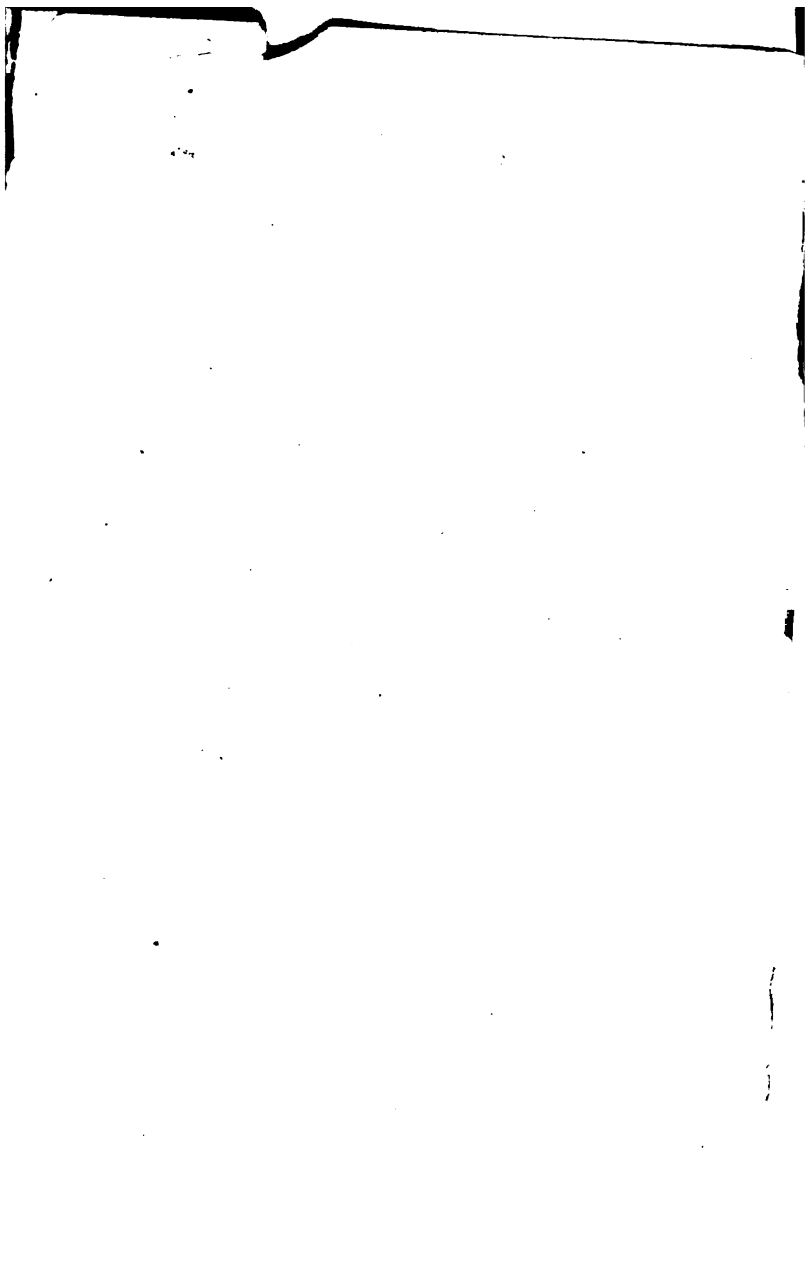
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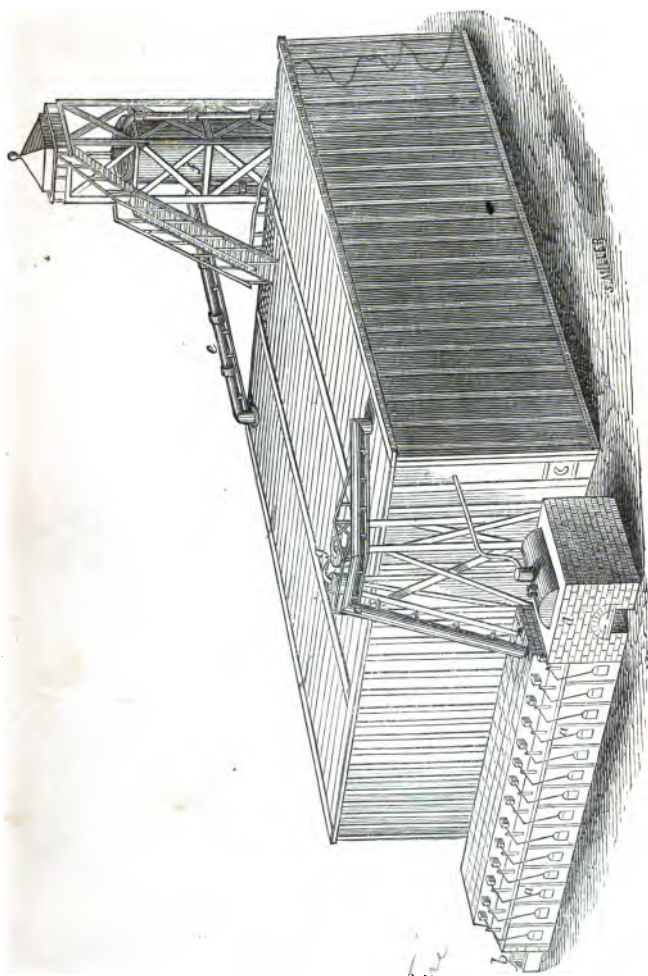


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See Fig.
SULPHURIC ACID CHAMBER.

Collins' Advanced Science Series.

A MANUAL
OF
INORGANIC CHEMISTRY.
VOL. I.
THE NON-METALS.

Thomas Edward BY

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NEW EDITION.

WITH COPIOUS INDEX AND EXAMINATION QUESTIONS AND EXERCISES.



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P R E F A C E.

IN attempting to make this work a faithful record of the present state of Inorganic Chemistry, the author found that the limits within which it was originally intended to confine it were quite inadequate to enable him to treat the subject with that fulness which seemed to him desirable. It has been decided, therefore, to extend the work over two volumes. The present volume treats of the Non-Metallic Elements and their compounds; the second will be devoted to the consideration of the Metals, and of those questions in Chemical Theory which, according to the author's experience, are most profitably discussed after the leading facts of the Science are made known. The more important Laws of Chemical Combination, and the main principles of the Atomic Theory are, however, considered immediately after the description of the Compounds of Oxygen and Hydrogen, in order that the student may understand the rational use of Symbolic Notation.

The author would here record his sense of the aid he has derived from the excellent series of Abstracts of British and Foreign Chemical Memoirs, published under the direction of the Chemical Society of London. This English "Jahresbericht" is simply invaluable to the compiler of a modern chemical text-book. The author is likewise greatly indebted to Mr. Henry Watt's admirable *Dictionary of Chemistry*. He desires, too, to express his obligations to his assistant, Mr. DUGALD CLERK, for the care with which he has revised the proof-sheets, and for the attention he has bestowed on the drawings for the figures; his thanks are also due to the engraver, Mr. STEPHEN MILLER, for the careful manner in which the wood-cuts have been executed.

GLASGOW, Nov., 1873.

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INORGANIC CHEMISTRY.

NON-METALS.

CHAPTER I.

1. Introduction.—The word Chemistry is derived from the Greek *χημεία* (*chemeia*), employed by certain writers in the beginning of the eleventh century to express “the art of making gold artificially”—a signification which we now attach to the word **Alchemy**. The root of the word is of doubtful origin. It is by some obtained from *Chemia*, an ancient name of Egypt, where the art is said to have originated. Some refer it to the Arabic *Kimia*, something hidden or secret; and others deduce it from the Celtic *Kheym*, fire. Even these do not exhaust the number of derivations which have been proposed.

2. Province of Chemistry.—When a candle burns in the air it gradually disappears, and the material of which it is composed passes away unseen. But is this material annihilated because it is no longer visible? Are we to suppose that when a body burns and disappears its substance is absolutely destroyed? We can only decide such a question by making the candle the subject of **experiment**; by carefully determining the precise condition under which it burns, and observing all the phenomena of its combustion. Experiment teaches us that if we burn it in a small confined space, say within a little bottle, the flame will languish, and sooner or later be extinguished; but that if we so arrange matters that the space in which the candle burns is practically unconfined, the candle continues to be consumed, and ultimately disappears. Now, if the candle required nothing to keep up its combustion, and gave off nothing in the burning to stifle its flame, there is no

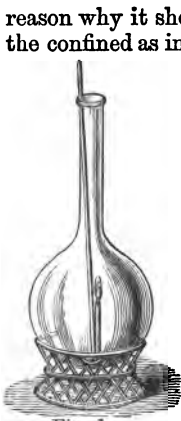


Fig. 1.

reason why it should not burn as readily and as completely in the confined as in the open space. Let us first determine if the candle gives off anything in burning. We bring it on the end of a wire into a clean and dry glass vessel (fig. 1), and allow it to burn there for a short time. We notice, almost immediately after its introduction, that the sides of the vessel are bedewed with moisture; and if, after withdrawing the candle, we pour in a clear solution of lime in water (lime-water), we observe that the liquid becomes turbid. It is scarcely necessary to assure ourselves that the candle, when not burning, and the wire, may remain together within the globe for any length of time without the glass being bedewed, or the air so affected as to render

lime-water turbid. Obviously, these effects are due to the combustion of the candle. As it disappears, water is produced, together with a gas which turns lime-water milky. Still our query—Does any annihilation of matter occur

when the candle burns? is not fully answered. We require to know whether the aggregate weight of the products of its combustion is equivalent to that of the candle burned. We must, therefore, so burn the candle that these products—the water and the gas which affects lime-water—can be collected and weighed. Fig. 2 represents an apparatus designed for this purpose. It consists of a wide glass tube, the upper half of which is filled with large

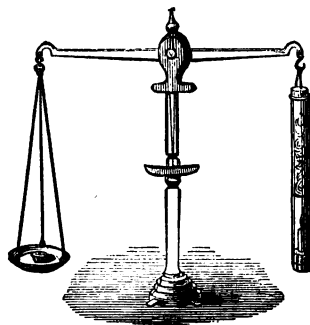


Fig. 2.

pieces of caustic soda resting on a few fragments of lime. The lime and soda are supported by a piece of stout

wire gauze pushed into the tube: they are intended to absorb the products of combustion. A cork fitting into the end of the tube, and pierced with holes, supports the candle: this may be of paraffin, a compound of carbon and hydrogen. The apparatus thus arranged is suspended from the end of a scale-beam, and is exactly counterbalanced. The cork is withdrawn, the candle lighted, and quickly replaced in the tube; it continues to burn rapidly, and without artificial aspiration if the spaces between the fragments in the tube are sufficiently wide. If a loss of matter occurs as the candle burns the apparatus must gradually decrease in weight; if, however, the weight of the products of combustion is equal to that of the candle consumed, the equilibrium will not be disturbed. But we see that as the candle diminishes the apparatus actually appears to *increase* in weight, and that the longer it burns, the greater is the deflection of the index. The soda and lime must therefore have absorbed *something* in addition to the constituents of the candle: that *something* is the substance derived from the air which supports the combustion of the candle. This gas, which we term oxygen, has combined with the constituents of the candle—with the hydrogen to form water, and with the carbon to form the gas, which affects lime-water, and to which we give the name of carbon dioxide. This experiment therefore demonstrates to us that when a body burns and disappears, its constituents are not destroyed, but pass into other combinations.

This fact admits of a variety of illustrations. If we inflame a piece of gun-cotton (a compound of carbon, hydrogen, oxygen, and nitrogen, containing a sufficient amount of oxygen to burn without air,) within an exhausted globe, it can be shown that the total weight of the invisible substances formed by the combustion is identical with that of the gun-cotton burned.

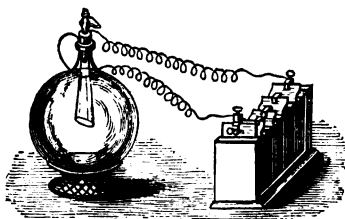


Fig. 3.

The globe (fig. 3) is closed with a caoutchouc cork fitted with a stop-cock; through the cork run two copper wires connected together at the end by a thin platinum wire wrapped round the piece of gun-cotton. The globe is exhausted by means of the air-pump, and accurately counterpoised whilst hanging on the arm of the balance. The thin platinum wire is then strongly heated by means of the electrical arrangement represented in the figure, and the gun-cotton thus fired. It completely disappears, but the weight of the apparatus remains absolutely unaltered. By innumerable repetitions of such experiments, the truth of the fundamental principle that matter is indestructible has been established. The sum of created matter is fixed and invariable. We cannot add anything to it, nor can we annihilate a particle of it. *This principle constitutes the basis upon which rests the whole superstructure of the science of Chemistry—that science which concerns itself with the study of the mutations of matter.*

3. Chemical Affinity.—In burning the candle or the gun-cotton, we have effected what is called a **chemical decomposition**. We have resolved these substances into others, possessing essentially different properties. That modification of force which brings about these changes—which causes the combination of the oxygen of the air with the carbon and hydrogen of the paraffin—is called **chemical affinity**. It is characteristic of this force to educe from a given body other substances differing altogether in properties from the original, or by causing the intimate juxtaposition of two substances, to produce a third body, essentially differing in properties from its components. The true nature of this action is as much hidden from the chemist as is the nature of gravitation. He can simply observe its effects, and attempt to discover the laws which regulate it. In seeking for these laws, he is led to inquire into the composition of all material things, and to study their action upon each other; to determine the conditions of their stability, and the circumstances under which they combine together; to estimate the proportions of the constituents in the resulting compounds; and to elucidate their *constitution*,

that is, to throw light upon the manner in which they are built up and held together.

In our earliest inquiries concerning this force, we notice that it cannot bring about union between all substances; thus, no combination of oxygen and fluorine is known to exist. Moreover, we observe that it is very unequally exerted between substances. The same body, fluorine, has such an intense chemical affinity for certain metals, and for silicon (an essential ingredient of glass and porcelain), that it is doubtful if it has yet been isolated. Chlorine and nitrogen exist together in such feeble combination, that the slightest action effects their disunion.

4. Modifying Influence of Chemical Affinity—Difference between Chemical Compounds and Mechanical Mixtures.—These substances, paraffin, gun cotton, water, &c., illustrate the remarkable modifying influence of chemical action. Carbon—a black shapeless substance, and hydrogen—a colourless invisible gas, when chemically combined, give rise to the transparent waxy-looking body paraffin. So oxygen and hydrogen, both colourless permanent gases, when chemically combined, form that most familiar of all liquids—water. These examples serve also to distinguish between the results of chemical action and mechanical admixture. By merely mixing oxygen and hydrogen in the proportion to form water, we cannot produce that liquid. In the mixture of the gases, the particles are in infinitely closer approximation than are the particles of the finest powder that we can obtain by mechanical means; and yet, even after the lapse of years, we can, by a suitable method, again separate the oxygen and hydrogen. But the two gases are ready to combine chemically with each other. If we simply bring a light to the mouth of the vessel in which they are confined, or allow a spark to pass into the midst of them, they unite with the greatest energy. If we intimately mix iron filings and flowers of sulphur together, we get a greenish-gray mass; but, although the colour of the mixture is sensibly different from that of either of its components, no such intimate union as that which chemical action effects has occurred. It is easy, by means of a lens, to discern that the particles of the sulphur are merely mixed with those of the iron; and by the

aid of a magnet, the whole of the iron may be separated from the sulphur. In fact, if the mixture be simply agitated in a large quantity of water, such a separation occurs, and the iron and the sulphur arrange themselves in accordance with their different specific gravities. But, if the mixture of iron and sulphur is heated, chemical combination occurs, and the mass is no longer attracted by the magnet; however finely powdered, sulphur cannot be discerned in it by means of a lens; nor do its constituents separate out on agitation with water. The iron and sulphur have combined chemically to form a third substance—ferrous sulphide—possessed of properties peculiar to itself. All the ingredients in mechanical mixtures can be separated by mechanical means; not so chemical compounds. We may reduce the ferrous sulphide to the finest possible state of subdivision, and yet each particle will be made up of ferrous sulphide, containing iron and sulphur in exactly the same proportion as in the original mass. The microscope affords us ample evidence of the extraordinary degree to which even the most complicated chemical compounds may be subdivided without their compound nature being destroyed. We know of animalcules so minute, that myriads of them can exist in a drop of water, and yet each possesses an organized structure, made up of many proximate substances, each of which is composed of many atoms of carbon, hydrogen, oxygen, and nitrogen. And still these microscopic animals assimilate the chemical compounds of phosphorus, calcium, magnesium, and oxygen contained in the water, in order to build up the inorganic structure of their tiny frames. The film of a soap bubble can be obtained of a thickness not exceeding one four-millionth of an inch; and yet this film consists of soap and water—the water being composed of oxygen and hydrogen; and the soap of stearic, oleic and margaric acids combined with soda, these substances being, moreover, composed of carbon, hydrogen, oxygen, and sodium.

Sir William Thomson, from certain lines of argument, which we cannot here enter into, has attempted to establish that in any ordinary liquid, transparent solid, or seemingly opaque solid, the mean distance between the centres of contiguous molecules is less than the hundred-millionth,

and greater than the two thousand-millionth of a centimetre. We may form some conception of the degree of coarse-grainedness thus indicated, if we imagine a rain-drop or a solid globe of glass to be magnified up to the size of the earth, when, if each constituent molecule were enlarged in the same proportion, the magnified structure would be coarser grained than a heap of small shot, but probably less coarse grained than a heap of cricket-balls.*

5. Elements and Compounds.—In subjecting all matter to his experiments, the chemist arrives at an ultimate division of substances into two great classes:—(1.) Elementary substances—bodies which he is unable to resolve into anything essentially different from themselves; and (2.) Compound substances—bodies which may be made to yield two or more essentially different substances. Thus, he is unable to make carbon yield any other kind of matter; nor can hydrogen, by any means at his disposal, be resolved into other substances. Carbon and hydrogen are therefore termed elements. On the other hand, paraffin is a compound; it is composed of carbon and hydrogen, into which substances it can be split up. So carbon dioxide is a compound; it is composed of oxygen and carbon. Water also is a compound; it is composed of oxygen and hydrogen. So also gun-cotton is a compound, since, by the action of heat, we have seen that it is decomposed, and its state permanently changed—we have resolved it into substances essentially differing from itself. The term element is to be understood with a certain limitation. As applied to any substance, it must be taken simply to mean that, up to the present time, no one has succeeded in decomposing that substance. Any such idea that these bodies are in their essence elementary, might lead us into error; for many substances, formerly supposed to be simple, are now known to be compounds; and no one can predicate that the substances we class among the elements to-day, will be ultimately found to be absolutely simple bodies.

The following is a list of the elements at present known to us. So far as we can tell, the entire universe is built up of these sixty-three elements and their combinations.

* *Nature*, p. 551, 1870.

6. List of the Elements, with their Symbols and Atomic Weights:—

Aluminium,	Al.	27.3	Molybdenum,	Mo.	96.0
Antimony (Stibium), ..	Sb.	122.3	Nickel,	Ni.	58.7
Arsenic,	As.	75.2	Niobium,	Nb.	94.0
Barium,	Ba.	137.2	Nitrogen,	N.	14.0
Bismuth,	Bi.	210.0	Osmium,	Os.	199.1
Boron,	B.	11.0	Oxygen,	O.	16.0
Bromine,	Br.	80.0	Palladium,	Pd.	106.6
Cadmium,	Cd.	112.0	Phosphorus,	P.	31.0
Cæsium,	Cs.	133.0	Platinum,	Pt.	197.2
Calcium,	Ca.	40.0	Potassium (Kalium), ..	K.	39.1
Carbon,	C.	12.0	Rhodium,	Rh.	104.2
Cerium,	Ce.	92.2	Rubidium,	Rb.	85.4
Chlorine,	Cl.	35.5	Ruthenium,	Ru.	104.4
Chromium,	Cr.	52.1	Selenium,	Se.	79.5
Cobalt,	Co.	58.7	Silver (Argentum), ...	Ag.	107.9
Copper (Cuprum),	Cu.	63.1	Silicon,	Si.	28.1
Didymium,	D.	95.0	Sodium (Natrium)	Na.	23.0
Erbium,	E.	112.6	Strontium,	Sr.	87.5
Fluorine,	F.	19.0	Sulphur,	S.	32.0
Glucium,	Gl.	9.3	Tantalum,	Ta.	182.3
Gold (Aurum),	Au.	196.7	Tellurium,	Te.	128.0
Hydrogen,	H.	1	Thallium,	Tl.	203.5
Iodine,	I.	126.9	Thorium,	Th.	115.7
Iridium,	Ir.	196.9	Tin (Stannum),	Sn.	118.1
Iron (Ferrum),	Fe.	56.0	Titanium,	Ti.	50.0
Lanthanum,	La.	92.9	Tungsten (Wolfram) ...	W.	184.0
Lead (Plumbum),	Pb.	206.9	Uranium,	U.	237.6
Lithium,	Li.	7.0	Vanadium,	V.	51.3
Magnesium,	Mg.	24.0	Yttrium,	Y.	61.7
Manganese,	Mn.	54.0	Zinc,	Zn.	65.2
Mercury (Hydrargyrum) Hg.	Hg.	200.0	Zirconium,	Zr.	89.6

7. Nomenclature of Elements.—The names of the elements are usually derived from some distinguishing feature or peculiarity. Thus, the name hydrogen (compounded of *υδρο*, *water*, and *γεννάω*, *I produce*) denotes that this gas is an essential constituent of water; thus, chlorine (from *χλωρός*, *yellowish green*) refers to the characteristic colour of the gas; thus, too, bromine (from *βρῶμος*, *a stench*) denotes that this substance possesses an irritating smell. Not a few, however, of the names have been arbitrarily chosen; thus, we have vanadium (from Vanadis, a Scandinavian deity); uranium, titanium, &c. Strontium, and yttrium, refer to the localities

where these elements were first discovered; lanthanum (from *λανθάνω*, to lie hid) alludes to the circumstance that this metal had previously been overlooked in the analysis of the mineral in which it was ultimately detected; didymium (from *δύμος*, a twin) refers to the fact that this metal was found to accompany lanthanum.

8. Nomenclature of Binary Chemical Compounds.—When two simple substances combine together, the name of the compound is generally formed from the names of its components. Thus—

Calcium and oxygen	form	Calcium oxide.
Sodium and chloride	„	Sodium chloride.
Hydrogen and sulphur	„	Hydrogen sulphide.
Magnesium and iodine	„	Magnesium iodide.

Occasionally it happens that two elements have the power of uniting with one another in different proportions. Thus, mercury forms two oxides; these are distinguished as mercurous oxide and mercuric oxide—the termination *ous* being given to the compound containing the least proportion of oxygen. Iron also forms two chlorides, which are designated as ferrous chloride and ferric chloride—the compound containing the larger proportion of chlorine receiving the terminal *-ic*.

9. Occurrence and Distribution of the Elements.—Comparatively few of the elements exist naturally uncombined. In the air we find oxygen and nitrogen; but the sea contains no simple substances beyond the constituents of air, whilst in the earth we find copper, silver, iron, gold, platinum, bismuth, mercury, sulphur, and carbon. By far the greatest amount of the earth's solid mass is made up of the combinations of the elements. It is found that silicon and oxygen in combination form upwards of two-thirds of the earth's crust—the remaining third being made up mainly of iron, aluminium, magnesium, calcium, carbon, sulphur, sodium, and potassium. A few of the elements, like oxygen, exist in great abundance; the others are far more sparingly distributed, and exist in few localities and in relatively small quantity. It is impossible, however, to draw any certain conclusions respecting the relative abundance of the elements, as our knowledge, even of the composition

of our own planet, is confined to a comparatively minute portion of it. Let fig. 4 represent a section of the earth drawn through its axis, then the relation of the fraction we have investigated to that yet unexplored would, in a circle of the diameter given in the figure, be represented by a line about $\frac{1}{15}$ th part of the thickness of that which forms its circumference. We thus see what little reason we have for believing that the number of the chemical elements in the universe is actually limited to sixty-three. Indeed, the very manner in which many of them have been discovered strengthens us in the belief that, as our means of research are increased, we shall add to their number. No sooner was electricity pressed into the service of chemistry than potassium, sodium, magnesium, calcium, strontium, and barium were added to the list; and immediately after the introduction of the prism into chemical research, caesium, rubidium, thallium, and indium were discovered.

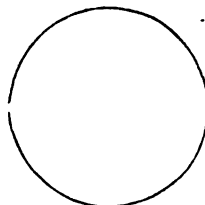


Fig. 4.

10. **Subdivisions of the Science.**—Chemistry occupies such an extensive sphere, its operations are so widely distributed, that it has been found desirable, for the greater convenience of study, to subdivide the matters upon which it treats. It was therefore agreed, as suggested by Lemery, nearly two hundred years ago, to divide the subject into the two branches of Inorganic and Organic Chemistry. **Inorganic Chemistry** was formerly defined to be the chemistry of the mineral kingdom, in contradistinction to **organic chemistry**, which was held to be the chemistry of the animal and vegetable kingdom, since most of the subjects included under this division were of animal or vegetable origin. This definition of Organic Chemistry is no longer tenable, for by far the greater number of the compounds classed by the chemist as organic are neither of vegetable nor of animal origin. Still, insensible as the real difference between them is, it is found convenient to retain the subdivisions on the score of expediency. As the substances hitherto comprised under the branch of Organic Chemistry invariably contain carbon, it has been decided to class with them the numberless carbon compounds which

have been subsequently discovered, and to study them in connection with one another. **Organic Chemistry** is to-day defined to be that portion of the science which treats of the preparation, properties, and constitution of the carbon compounds.

The bodies treated under Inorganic Chemistry are divided into two principal classes—**Metals** and **Non-metals**. This division is also perfectly arbitrary; there exists no absolute line of demarcation between the two branches, and we are unable to say precisely what constitutes a metal, and what a non-metal. It thus happens that chemists are not agreed in the arrangement of the elements in these subdivisions. Thus, to some, the high specific gravity and bright metallic lustre of arsenic are sufficient reasons for classifying it among the metals; to others its marked chemical analogies to phosphorus and nitrogen (which all are agreed to regard as non-metals), its great brittleness, and low conductivity for heat and electricity, are arguments for assigning it a place among the non-metals. But arsenic has a distinct chemical relationship to antimony, which is universally included among the metals; whilst brittleness, and a low conducting power for heat and electricity are common to many elements invariably regarded as metals. In this work the following substances will be studied under the division of the non-metals :—

Arsenic.	Fluorine.	Phosphorus.
Boron.	Hydrogen.	Selenium.
Bromine.	Iodine.	Silicon.
Carbon.	Nitrogen.	Sulphur.
Chlorine.	Oxygen.	Tellurium.

The remaining elements will be considered under the division of the metals.

11. Analysis and Synthesis.—The chemist determines the ultimate composition of compounds, either by resolving them into their elements, or into certain well known combinations of those elements. Thus, he may determine the composition of magnesium carbonate (a compound of magnesium, carbon, and oxygen), by extracting these elements from it; or he may split it up into carbon dioxide and magnesia, which substances he knows, by previous experience, to be respectively composed of carbon and oxygen, and magnesium

and oxygen. Such a process of decomposition, made with the object of ascertaining the components of a body, is termed an **analysis**. If the chemist merely inquires what substances are present in the compound, or the mixture, he is said to make a **qualitative analysis**; if he proceeds to determine the relative proportions of the constituents, he makes a **quantitative analysis**. Occasionally the composition of a body is determined by a method diametrically opposed in principle to that of analysis—that is, by bringing the constituents together, and effecting their combination; such a process is termed **synthesis**. Thus, we may determine the composition of water by resolving it into oxygen and hydrogen; or we may bring the oxygen and hydrogen together under such conditions that they combine to form water. In the one case we make an analysis; in the other a synthesis. As examples of these contrasted processes, we may perform the following experiments:—Bring a small portion of the red powder known as mercuric oxide into a dry test-tube, and heat it strongly over the lamp (fig. 5), it rapidly darkens in colour, and a lustrous mirror forms on the colder portion of the tube. If we bring a glowing

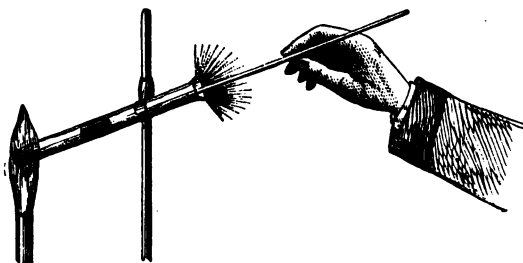


Fig. 5.

splinter of wood into the heated test tube, it bursts into flame, and continues to burn vividly. The invisible gas which thus supports combustion so energetically is oxygen, and the bright mirror on the glass consists of exceedingly fine globules of mercury or quicksilver. We have thus resolved the mercuric oxide into its constituents—we have proved it, by analysis, to consist of mercury and oxygen.

But we can satisfy ourselves of the composition of mercuric oxide by synthesis—that is, by showing that the liquid metal, mercury, and the invisible gas, oxygen, can combine together to form the red powder mercuric oxide. A small quantity of mercury is heated, nearly to boiling, in a long-necked flask, to which a glass tube is attached, as in fig. 6. After some hours heating, the surface of the metal becomes covered with a reddish film of mercuric oxide, which, on shaking, adheres to the side of the flask, and may thus be separated from the unaltered mercury.*

12. Chemical Symbols and Formulæ, Atomic Weights.—It will be observed that in the foregoing list of elements a distinctive letter, or letters, is attached to each member; these are termed **chemical symbols**. In general they consist of the initial letters of the elements to which they refer. Not unfrequently, however, several elements are found possessing the same initial letter; in such cases we assign the single letter to the most abundant or important, or earliest discovered member of the series, and to the others we add a second and distinguishing letter. Thus no fewer than seven names of elements commence with C. We reserve the single letter for Carbon, unquestionably the most important of the number; Calcium therefore becomes Ca; Cadmium, Cd; Cerium, Ce; Chlorine, Cl, and so on. A few of the elements have symbols which do not contain their initial letter; thus, Fe stands for iron, and Pb for lead. With a few exceptions,

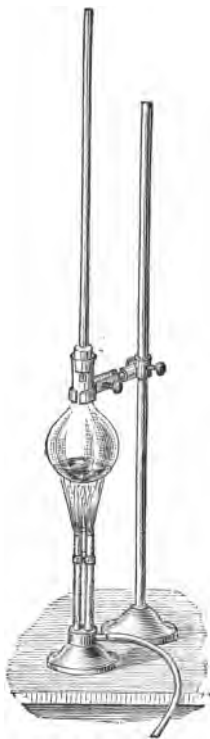


Fig. 6.

* Care must be taken so to conduct this experiment that any mercurial vapours which escape condensation may be carried away from the experimenter.

which will be pointed out hereafter, the bodies to which these irregular symbols are attached were known to the ancients, and the symbols are derived from the names by which they were called.

In the same manner we may represent compound bodies by means of symbols; thus, HgO stands for mercuric oxide, which we have already learned consists of mercury (Hg) and oxygen (O).

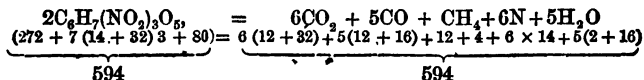
But these symbols possess a quantitative as well as a qualitative signification. Hg does not represent an indeterminate quantity of mercury, nor O an indefinite amount of oxygen. Hg invariably means 200 parts of mercury, and O 16 parts of oxygen. HgO , standing for mercuric oxide, always signifies 216 parts of that body, and, moreover, implies that it is made up of 200 parts of mercury, combined with 16 parts of oxygen. Thus, too, FeS , standing for ferrous sulphide, always denotes 88 parts of that body, and tells us at the same time that it is made up of 56 parts of iron united to 32 parts of sulphur. The numbers expressing these relations among the elements are termed their **combining or atomic weights**, and they are all referred to that of hydrogen as unity, since this substance is found to possess the lowest atomic weight.

The atomic weights of the elements express their weights when in the state of gas, and occupying, under similar conditions of temperature and pressure, the same volume as one part by weight of hydrogen. One gram of hydrogen occupies a space of 11.19 litres at 0° and 760 m.m. pressure; the same space would be occupied at the same temperature and pressure by 16 grams of oxygen, or 14 grams of nitrogen, or 35.5 grams of chlorine. But by far the greater number of the elementary bodies cannot be vaporized at temperatures which we can measure, and accordingly their atomic weights are deduced from other considerations. It is found by experiment that a certain relation exists between the atomic weight of an element in the solid state, and the amount of heat required to raise it through a given interval of temperature. This may be thus expressed—"Specific heat \times atomic weight = constant." With a very few exceptions, the atomic weight of an element in the solid condition is the weight of that element which at any given temperature contains the

same quantity of heat as seven parts by weight of solid lithium at the same temperature. We shall have occasion hereafter to return to this subject of the atomic weights of the elements.

By the addition of numbers, placed after the elements to which they refer, we may cause this symbolic language to express the composition, even of the most complex chemical compounds. Thus CO_2 , representing carbon dioxide, denotes 44 parts of that body, and informs us that it is composed of 12 parts of carbon combined with 16×2 or 32 parts of oxygen. So also H_2O , denoting water, means 18 parts of this substance, and implies that it is made up of oxygen and hydrogen in the proportion of 16 parts of the former to 2 parts of the latter. 2 (CO_2) would of course mean 2 (12 + 32), or 88 parts of carbon dioxide; and $\text{C}_6\text{H}_7(\text{NO}_2)_3\text{O}_8$, representing the composition of gun-cotton, denotes that this body is composed of 72 parts of carbon, 7 of hydrogen, 42 of nitrogen, and 176 of oxygen. Such an allocation of symbols is termed a **chemical formula**.

13. Chemical Equations.—By means of chemical formulæ the chemist can express concisely the action of substances upon one another, and also represent both the nature and the quantity of the products into which a given body is decomposed. Such symbolic expressions of chemical reactions are termed **chemical equations**. The sign + placed between two symbols or formulæ denote that the bodies are mixed together, or are produced in conjunction. The sign = is used in the sense of “produces” or “yields,” and only retains the meaning of equality in so far as it indicates that the aggregate weight of the products of a chemical reaction is identical with the original weight of the reacting materials. If we assume that the decomposition of gun-cotton on ignition may be represented by the equation—*

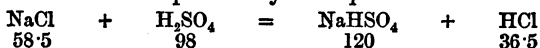


we imply that 594 grams of gun-cotton will give—

* This representation of the decomposition is not strictly, although very nearly, true.

Carbon dioxide (CO ₂),.....	264	grams.
Carbon monoxide (CO),.....	140	"
Marsh gas (CH ₄),.....	16	"
Nitrogen (N),.....	84	"
Water (H ₂ O),.....	90	"
	<hr/>	
	594	grams.

When we add sulphuric acid (H₂SO₄) to common salt, or sodium chloride (NaCl), we obtain sodium-hydrogen-sulphate (NaHSO₄), and hydrochloric acid gas (HCl). This decomposition would be expressed by the equation—



which means that 98 grams of sulphuric acid, when mixed with 58.5 grams of sodium chloride, yield 120 grams of sodium-hydrogen-sulphate, and 36.5 grams of hydrochloric acid gas. The sign = is here used in a sense different from that of the mathematicians, in that it does not imply that the two sides of the equation can be transposed; thus, in this case we cannot say that $\text{NaHSO}_4 + \text{HCl} = \text{NaCl} + \text{H}_2\text{SO}_4$. By the aid of the first equation, we can readily calculate how much salt and sulphuric acid would be needed to produce a given weight of hydrochloric acid gas, and how much sodium-hydrogen-sulphate would remain.

CHAPTER II.

14. Weights and Measures.—Before we proceed to make these and similar calculations, it will be desirable to explain the principles of the system of weights and measures which we intend to use. By reason of its simplicity and convenience, the French metrical system has commanded almost universal acceptance among scientific men. Its advantages are causing it to be rapidly adopted, even by the governments of countries already possessed of a carefully defined national system. This system was authorized in France, in 1795, by law of the First Republic. A rod of platinum was constructed, and the distance between its ends, measured when the rod was

at the temperature of melting ice, was adopted as the standard of length, and styled a *metre*. This rod of platinum was intended by the French geometricians who planned the system to represent the one ten-millionth part of the distance from the equator to the pole, measured along the earth's surface. But, by a careful revision of the geodetical observations required to determine this distance, it has been shown that the metre as originally defined exceeds the metre as actually constructed by about $\cdot 0000086$ m.; or that the distance from the equator to the poles, instead of being 10,000,000 times, is actually 10,000,086 times the length of the platinum bar.

The metre is, therefore, as much an arbitrary standard of length as our own yard, which, as enacted by Parliament, is the distance, measured at 62° F., between the centres of the transverse lines in two gold plugs in a bronze bar deposited in the Exchequer Office. The value of the French metrical system depends upon the fact that the multiples and sub-multiples of its units are connected together by a decimal system of multiplication and division. Thus, the *decimetre* (d.m.) is the tenth part of a metre; the *centimetre* (c.m.) is the hundredth part; and the *millimetre* (m.m.) the thousandth part. The prefixes of the subdivisions are of Latin origin. To express the higher multiples, Greek prefixes are employed. Thus, ten metres make a *deca*-metre; a hundred metres, a *hecto*-metre; and a thousand metres, a *kilo*-metre. The kilometre is used on the continent as a measure of distance by road. It is about five-eighths of our mile. The metre is a little over $\frac{1}{4}$ yard, or, more exactly, 39.37 inches; hence 10 c.m. are rather less than 4 inches, or 25 m.m. make nearly 1 inch.*

The unit of *capacity* of this system is the cube of one decimetre, and is termed a *litre*. This is equal to 1,000 cubic centimetres (c. c.), and is rather more than $1\frac{1}{4}$ imperial pints; more exactly, 1.76 pints, or 61.03 cubic inches.†

* To reduce millimetres to inches—

$$\text{Log. m.m.} + 2.59516 = \text{log. inches.}$$

To convert inches to millimetres—

$$\text{Log. in.} + 1.40483 = \text{log. m.m.}$$

† To reduce cubic centimetres to cubic inches—

$$\text{Log. cub. c.} + 2.78550 = \text{log. cub. inches.}$$

To convert cubic inches into cubic centimetres—

$$\text{Log cub. in.} + 1.21450 = \text{log cub. c.}$$

The system of **weights** is connected with that of capacity and of length by assuming as the unit the weight of 1 cubic centimetre of pure water, at a temperature of 4° C. This weight is styled a gram (grm.), and it is equal to 15·432 grains. Its most commonly used multiple is the kilogram (kilo.), which contains 1,000 grams; it is the commercial unit, and is about 2½ British pounds. It may be convenient to remember, that 1,000 kilos. or 1 cubic metre of water, is very nearly equivalent to an English ton. The reason for the adoption of the temperature of 4° C., in the determination of the weight, will be explained hereafter. This system of weights is perfectly arbitrary, inasmuch as it depends upon certain experimental data, about which there is no absolute agreement between observers. The standard of mass is a certain piece of platinum, preserved in Paris, and called a kilogram, of which copies are made by direct comparison. If all these copies were lost, it is doubtful if a kilogram could be reproduced of exactly the original weight.*

15. The Balance.—This instrument is of inestimable value to the chemist—he constantly appeals to its indications. Mechanicians have accordingly devoted much labour to render it as perfect as possible, and there are few instruments of precision which rival the modern chemical balance in the accuracy of their work. Fig. 7 represents one of the forms of this instrument. It consists of a perforated brass beam, suspended at the centre on a triangular piece of hardened steel or agate, termed a *knife-edge*, which oscillates on a polished plate of agate, fixed on a brass support. At each end of this beam is fixed a similar knife-edge of agate or steel, on which rest two agate plates, imbedded in brass settings. From each of these a hook depends, to which the pans are attached by light wires or thin straps. Figs. 8 and 9 give enlarged representations of these terminal knife edges and planes. When the instrument is not in use, the beam rests upon a frame connected with a rod, which descends through the pillar of the balance, and which

* To reduce grams to grains—

$$\text{Log. grams} + 1.18843 = \text{log. grains.}$$

To convert grains into grams—

$$\text{Log. grains} + 2.81157 = \text{log. grams.}$$

can be raised or lowered by an eccentric. The same movement also lifts up the plates connected with the pans, so

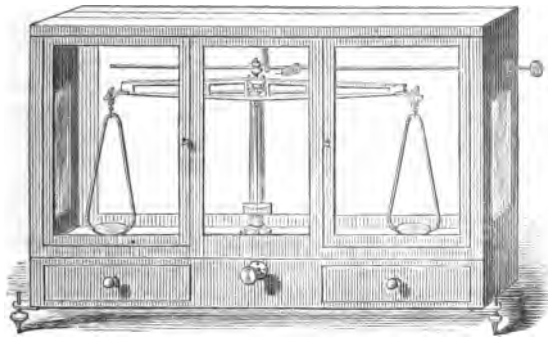
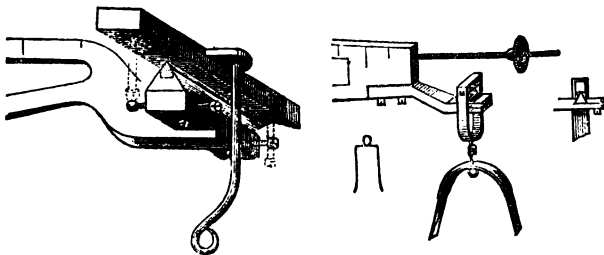


Fig. 7.

that the knife edges and agate planes are only in contact when the balance is oscillating. A second eccentric, con-



Figs. 8 and 9.

nected with two bent levers, raises or depresses a support under each of the pans, so that they may be kept stationary whilst their load is being placed on them, or their vibrations arrested before the beam is lowered down on the centre plate. In some balances all these movements are so connected, that a single turn of the eccentric first rapidly releases the supports of the pans, then gently lowers the beam upon the centre knife-edge, and finally drops the pan suspensions

upon the terminal knife-edges. By these arrangements, the durability of the instrument is greatly increased.

To the beam is attached a long index, or pointer, moving before a graduated scale fixed to the pillar of the balance. This renders visible the slightest oscillations of the beam. So long as the instrument is in equipoise, the pointer hangs perfectly vertical, and opposite to the middle (zero) point of the scale, or oscillates over an equal number of divisions on each side. The least preponderance on one side is indicated by a permanent deflection of the pointer from the zero, or by its vibrating through an unequal number of divisions on either side of the zero point. If from any cause the instrument itself is not in equilibrium, it may be adjusted by means of a little movable vane, fixed on the top of the beam, by moving which, either to the right or left, the preponderance may be counterpoised. In some balances, in which the pans are suspended by a simpler method, this adjustment is effected by means of a little milled-head screw travelling along a thread. (Fig. 9.)

The *accuracy* of the balance depends—(1.) upon the equality of its arms; (2.) upon the position of the point of support in relation to the centre of gravity of the instrument; from which also follow (3.) that the points of suspension and support must be in the same plane; and (4.) that the beam must be perfectly rigid.

The *sensibility* of the instrument depends—(1.) upon the freedom from friction between the knife-edges and planes; (2.) upon the near approximation of the centre of gravity of the instrument to its point of support; and (3.) upon the lightness of its beam.

The relation of the centre of gravity to the point of support is of course adjusted as accurately as possible by the maker; but, by means of a little weight (termed a gravity-bob), working on a thread, it may be altered at will, and the stability of the balance thus regulated. It will be obvious that an instrument capable of such refinement is liable to be affected and its delicacy impaired by many extraneous causes. As one means of preservation, and of preventing its indications being affected by currents of air, the balance is always kept in a glass case. A good balance will indicate one part in a

million; when loaded with one hundred grams in each pan it will *turn* by the addition of $\frac{1}{10}$ of a milligram.

In weighing, the same pan should invariably be employed for the same purpose—that is, the body to be weighed must always be placed on one and the same pan, which may be termed the object-pan, in contradistinction to that on which the weights are placed, which may be termed the weight-pan. The *ratios* of the weights in the course of an analysis are thus preserved, even when the arms of the instrument are not perfectly equal; and as the chemist mainly concerns himself with the ratios of weights, and not, as we commonly say, with absolute weights, the defects of the instrument as constructed are compensated. The true weight of an object may, however, be obtained either by the **method of reversal**, or by that of **substitution**. In the method of reversal the object is weighed first in one pan and then in the other. If the weights are identical, the true weight of the object is at once given. If the weights, from inequality in the arms, are unequal, their geometric mean will be the true weight; this is found by multiplying the apparent weights together, and extracting the square root. If their difference, however, is inconsiderable, their common arithmetic mean will be very nearly the true weight. In the method of substitution we place the object to be weighed, *X*, on one pan, and equipoise it by a counterpoise *W*; we then remove *X*, and substitute weights, *W*, until equilibrium is restored. Obviously $X = W$, although both may differ from *W* by an unknown amount. The substance to be weighed, say a crucible, is placed upon one pan, and the equilibrium adjusted by adding small shot, tinfoil, or pieces of wire to the other pan. The crucible is removed, and weights are placed in its stead, until the balance is again in equilibrium. The true weight of the crucible is expressed by the aggregate values of the weights substituted. The determination of equality is made by means of the pointer; if it oscillates through an equal number of scale divisions to the left and right of the zero, the weights are in equilibrium. If we take the mean position from a series of such oscillations, and know the weights corresponding to the various deviations from the zero point of the pointer, we can determine the true weight of a body with a close approximation to accuracy. On account of the conditions which they require in the balance

and balance room, and the length of time which they need, such refined methods of weighing are only resorted to in determinations of the combining weights of the elements, and of certain physico-chemical constants.

Obviously all methods of weighing by means of weights demand that the multiples and sub-multiples of the unit weight really bear the ratios which they represent. Thus the 10-gram piece in a set of weights must be really 10 times the weight of the 1-gram piece, and the centigram weight the one ten-thousandth part of the 100-gram weight. It is not of so much importance, although it is certainly convenient, that the gram should be exactly the thousandth part of the standard kilogram preserved at Paris, so long as the other denominations of the set truly bear the ratios impressed upon them. Various substances have been proposed, on the score of their durability, for the material of weights; and platinum, by reason of its power of resisting corrosion, seems especially applicable; but in general the weights consist of small cylinders of gilded brass, furnished with little handles, to enable them to be conveniently transferred, by means of small forceps, backwards and forwards from the box to the balance pan. The weights are hollow beneath the handle, to receive small pieces of wire or foil, by the addition of which they are adjusted. The smaller weights are made of platinum, and sometimes of palladium or aluminium foil. Fractional parts of the centigram are generally determined by means of a little piece of bent wire, weighing 1 centigram, termed a rider (fig. 8), which, by the aid of the brass sliding-rod and movable arm, can be conveniently placed upon one arm of the balance beam. This is divided from the centre to the pan-suspension into 10 equal parts, each equivalent to 1 milligram, and each of these parts is further subdivided into 5 equal parts, equivalent to 0.2 milligram. When placed on the pan, or immediately over its point of support, the rider weighs 1 centigram; when placed half-way between the centre support and the pan-suspension, it is equivalent to 0.5 centigram, or 5 mg.; when placed a fourth of the way, it indicates 0.25 centigram, or 2.5 mg.; and so on.

But the determination of the true weight of a body is not merely dependent on the use of an accurate balance and weights. It is affected by the presence of the air in which the weighings are made: the magnitude of the error from this

cause is proportionate to the difference between the volume of the weights and of the body weighed. If the volume of the body is greater than that of the weights, its weight, as indicated by the balance, is too small; and, conversely, when the volume is less than that of the weights, the indicated weight is too great. In the generality of cases the error thus introduced is too small to be taken cognizance of in ordinary determinations of weight, but in normal determinations it is never neglected. It is worthy of remark that the use of weights of a medium specific gravity, such as brass, tends to obviate the frequent necessity of correcting the indications of the balance for this source of error: if platinum (sp. gr. 21) on the one hand, or quartz (sp. gr. 2.5) on the other, were employed as the material of weights, the correction would be more frequently required. A method of obviating the necessity of correction for air displaced will be described in a subsequent section. The operation of weighing is attended with many other sources of error which cannot here be described; but the student will have gleaned that the determination of the accurate weight of a body is a problem of no slight difficulty.

16. The Thermometer.—Heat is one of the chief agents which set up chemical action. It is necessary, therefore, that the chemist should possess the means to estimate its amount and intensity. Instruments designed to measure the quantity of heat are termed **calorimeters**; those intended to estimate its intensity are called **thermometers**. At present we shall occupy ourselves only with the study of the construction and use of the latter class of instruments. The intensity of heat is usually measured by its effect in altering the volume of certain substances. Of what are usually termed the three physical states of matter, the one most generally applicable to thermometric purposes is the liquid, as gases expand too much and solids too little to be generally employed. Of all liquids yet proposed the most suitable is mercury, which admits of the measurement of a great range of temperature, as its boiling and freezing points are widely separated: it expands in a uniform manner—i. e., equal increments of heat affect it at a low temperature nearly as much as at a high temperature; it does not adhere to glass, has a low capacity for heat, and is easily obtained in a state of purity. To make a mercurial thermometer, a perfectly clean capillary glass tube of circular

or elliptical bore is chosen, and the uniformity of this bore is tested by propelling a short column of mercury along the tube, and determining if its length is invariable in different positions. It is generally found that the column of mercury becomes either gradually shorter or longer, indicating that it increases or diminishes regularly in diameter from end to end. In very accurate instruments these differences are taken into account: the degrees are either modified in accordance with the increment or decrement in diameter, or they are made of uniform size, and the indications of the thermometer corrected by the use of a factor representing the variation. One end is now sealed and softened in the blowpipe flame and blown out into a bulb, by means of a small elastic ball fixed on the open end, and compressible by the hand. The



shape of the bulb depends upon the purpose for which the thermometer is intended. In chemical thermometers the bulb is usually cylindrical or tubular, and is generally of smaller outward diameter than the stem, so that the instrument may be readily and without risk pushed through the hole in a cork. A bulb of this shape exposes a large surface for the transmission of heat, and thus adds to the sensitiveness of the instrument. The walls of the bulb must not be too thick, on account of the badly conducting nature of glass; nor must they be too thin, or they will yield to atmospheric pressure, and render the capacity of the bulb variable.

To fill the instrument, a wider tube of glass is attached to the stem by a cork (fig. 10), and a quantity of pure dry mercury, more than sufficient to fill the bulb and stem, is poured into it. The bulb is gently heated, and a portion of the air is thus expelled, which bubbles up through the mercury. As the volume of the remaining air contracts on cooling, the mercury is driven into the instrument, and falls in minute drops into the bulb. The bulb is again heated, and again allowed to cool, when a fresh portion of mercury enters, and this process is repeated until the bulb is nearly full. By heating the metal in the bulb to boiling, its vapour expels the last traces of air and moisture, and, on cooling, the reservoir and tube become completely filled. The wider tube is now removed, and the

entire instrument heated slightly above the highest point that it is intended to measure. The excess of mercury is thus expelled. After a momentary cooling of the tube, its end is dexterously sealed by means of the blow-pipe flame. As the mercury cools and contracts, the space above it is left vacuous, with the exception of a minute quantity of mercurial vapour which pervades it. The space above the column of mercury is therefore free from anything which can modify its expansion.

The perfection of the vacuum is easily ascertained by inverting the instrument and, if necessary, gently tapping it, when the mercury ought to fill the capillary portion completely.

17. Method of Graduating the Thermometer.—In its present form the instrument could only be used as a thermoscope—that is, it could tell us whether one liquid was hotter than another, or whether one day differed in temperature from the next. It would even inform us that water boiled at a lower temperature on the top of a mountain than at the bottom, and that ice melted at the same temperature both at the top and bottom; but its indications would not be comparable with those of any other instrument, since they would possess no common fixed points of comparison. The earliest instruments suffered under this disadvantage, and their indications were therefore comparatively valueless. Newton proposed that the temperatures of melting ice and of steam from boiling water (which had previously been shown to be fiducial points) should be used in the graduation of thermometers, and these fixed points are now universally employed. The instrument is first placed in melting snow or ice (fig. 11), and, when the mercurial column is stationary, its position is marked by a scratch upon the stem, and styled the freezing point. The tube is now transferred to the metallic vessel represented in fig. 12, in which it can be entirely immersed in steam. When the position of the column is once more constant, its height is again marked on the stem, and, for a reason to be hereafter mentioned, the height of the barometer is simultaneously read off. The space between the two marks is then divided into a certain number of divisions, termed degrees, which are in the best instruments etched upon the stem, the graduation being extended above and below the fixed points. The number of these divisions un-

fortunately varies in different instruments: the simplest plan is to divide the space in 100 parts or degrees, calling the

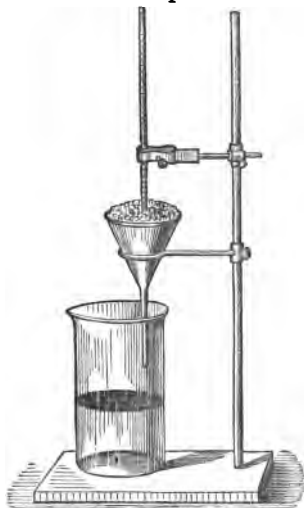


Fig. 11.

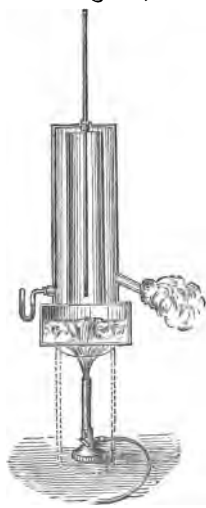


Fig. 12.

freezing point zero (0°), and the boiling point 100° . This mode of subdivision was proposed by Celsius, and is termed the centigrade scale: it is generally employed by scientific men, and will be invariably used in this work. In the scale of Fahrenheit the interval is divided into 180 degrees, but the zero point is placed at a distance of 32 of these degrees below the freezing point; hence the boiling point on this scale is $180 + 32$, or 212° . The scale of Reaumur is divided into 80 parts, the zero being at the freezing point; accordingly, water boils at 80° Reaumur. The conversion of degrees from one scale to the others is easily made by means of the following formulæ (C., centigr.; F., Fahr.; R., Reau.):—

F. $^{\circ}$ to C. $^{\circ}$; $\frac{5}{9}$	(F. $^{\circ}$ - 32) = C. $^{\circ}$.
C. $^{\circ}$ to F. $^{\circ}$; $\frac{9}{5}$	C. $^{\circ}$ + 32 = F. $^{\circ}$.
R. $^{\circ}$ to F. $^{\circ}$; $\frac{9}{4}$	R. $^{\circ}$ + 32 = F. $^{\circ}$.
F. $^{\circ}$ to R. $^{\circ}$; $\frac{4}{9}$	(F. $^{\circ}$ - 32) = R. $^{\circ}$.
C. $^{\circ}$ to R. $^{\circ}$; $\frac{4}{5}$	C. $^{\circ}$ = R. $^{\circ}$.
R. $^{\circ}$ to C. $^{\circ}$; $\frac{5}{4}$	R. $^{\circ}$ = C. $^{\circ}$.

The determination of the true temperature of a body is as

difficult a problem as the determination of its weight, and the indications of the thermometer need a number of corrections whenever the greatest possible accuracy is desired. The method of determining the true boiling point of a liquid may serve as an example of the care and number of precautions required in the accurate estimation of temperature. The liquid, the boiling point of which is to be determined, is placed in a small distilling flask (fig. 13), which is connected by means of the lateral tube with a condensing arrangement, to prevent loss of the substance; the thermometer is supported in the neck of the flask by a cork, in such a manner that the bulb, and as much of the stem as possible, shall be immersed in the vapour of the substance. In order to insure

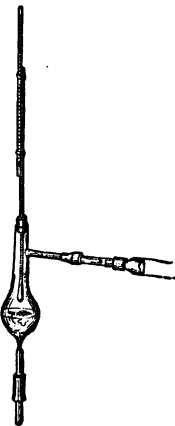


Fig. 13.

regular ebullition, a few pieces of platinum foil or wire are introduced into the flask. The liquid is then heated by a small flame, and when in full ebullition, the height of the thermometric column is noted. Call this T . In the generality of cases, a portion of the column rises above the cork, and is, therefore, surrounded by air of a lower temperature than that of the heated vapour. The boiling point, as thus indicated, is, therefore, lower than the true boiling point of the liquid in proportion to the length of the column thus cooled. In order to correct the *reading* of the thermometer, it is necessary to know the mean temperature of the column above the cork; this may be determined with sufficient accuracy by attaching a second thermometer to the stem of the other, in such a manner that its bulb is mid-way between the cork and the top of the heated column. Call this mean temperature t . If we further note the number (N) of degrees on the scale of the mercurial column, not directly heated by the vapour, and know the apparent expansion of the mercury in the glass, δ , we can determine the correction to be added to the indication T of the thermometer. It is found by the formula—

$$N (T - t) \delta.$$

δ varies with the nature of the glass of the instrument, but may be taken with sufficient accuracy at 0.00155. In experimenting with liquids possessing high boiling points, a considerable portion of the mercurial column may be unexposed to the vapour; in such cases, the correction to be added may amount to several degrees.

Before, however, the experimenter makes such a normal determination, he assures himself that the real zero point of his instrument is known to him. In practice it is found that the zero point as marked on a thermometer rarely coincides with the temperature of melting ice, and, generally speaking, the older the instrument, the greater is the variation. This is due to no fault of the maker, but to a gradual molecular change in the material of the envelope, which goes on long after the instrument is made, whereby the capacity of the reservoir is diminished.* After the thermometer has been heated, its zero invariably falls; on the other hand, after having been cooled to a very low temperature, it rises slightly. These variations, when compared with the permanent change above mentioned, are but temporary: in a few hours the reservoir acquires its original volume. For these reasons, in fine thermometers, the zero is determined some months after the mercury is introduced and the tube sealed. We also see from this why the freezing point is directed to be determined before the boiling point.

To redetermine the zero, the thermometer is simply immersed in melting snow or ice, and, after a sufficient interval, the position of the mercury is read off on the scale (fig. 11, p. 34). The 100° point is also redetermined by means of the apparatus represented in fig. 12, p. 34. Let us suppose that the ice melted apparently at + 0.4 on a certain instrument, and that water apparently boiled at 101°, the barometer being exactly at its mean height at the sea's level. Then

$$1^{\circ} \text{ C.} = \frac{101.0 - 0.4}{100} = 1.006^{\circ} \text{ of our thermometer.}$$

Suppose, too, that in determining the boiling point of a liquid with this thermometer, we had obtained the following data:— $T = 79.2$, $N = 40$, $t = 30$. Then $79.2 + 40(79.2$

* Dr. Joule has traced this rise in the zero point of a thermometer in his possession during twenty years, and he finds, even after this period, that the capacity of the bulb is not constant.

$- 30) \cdot 000155 = 79 \cdot 5$, and $\frac{79 \cdot 5}{1 \cdot 006} = 79 \cdot 0^\circ \text{C}$, the true boiling point of the liquid.

Ordinary thermometers are of course inapplicable to the determinations of temperatures above the boiling point of mercury. Berthelot has proposed a very simple apparatus (fig. 14) for the estimation of temperatures above 300° , which permits of a tolerably close approximation to exactness. It consists essentially of a glass or silver reservoir filled with air, connected with the bent glass tube by a capillary tube, which is partially filled with mercury. The instrument is supported by a stand, to which is attached a movable double scale, which can be clamped in any desired position. Mercury is poured into the bulb, and by means of an air-pump the in-

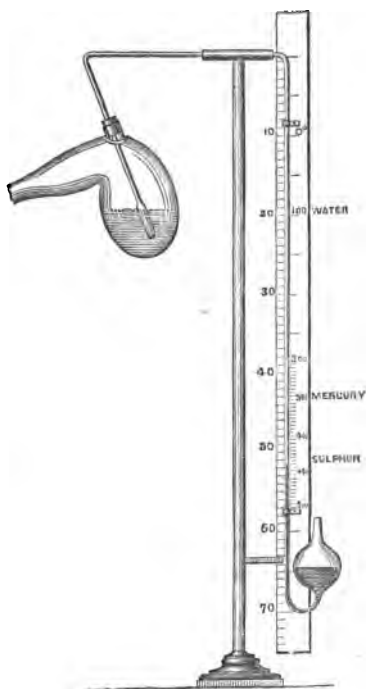


Fig. 14.

strument is partially exhausted; on restoring the pressure, the mercury is driven to a certain distance up the vertical tube. The thermometer is graduated by immersing the bulb into melting ice; the air within the bulb of course contracts, and the mercury rises within the tube; the point to which it ultimately attains constitutes the zero of the instrument. The bulb is then surrounded by the steam from boiling water, and the position to which the mercury now sinks marks the 100° point. The bulb is next

brought into an atmosphere of mercurial vapour, evolved from the boiling metal; the point at which the height of the column again becomes constant is styled 350°. Lastly, the bulb is surrounded with the vapour of boiling sulphur, and the point to which the column is depressed is marked 440°. The intermediate temperatures, together with those above 440°, are obtained by extra—and interpolation. Since the *modus operandi* of the instrument depends upon the tension exerted by the confined volume of air, this graduation is only applicable when the atmospheric pressure happens to be identical with that at the time at which it was made. Whenever a measurement of temperature has to be made under a different pressure from the initial one, the zero must be redetermined by surrounding the bulb with melting snow or ice, and making the 0° on the movable scale to coincide with the extremity of the mercurial column. This instrument is not theoretically faultless, but it will estimate temperatures in the neighbourhood of 500° with a probable error of 3°.

For other methods of determining temperature, larger manuals must be consulted.*

18. Relation of the Volumes of Gases to Temperature and Pressure—the Barometer.—Before entering on the study of the gases, it is advisable to describe the methods of measuring the pressure of gases, since their densities are materially influenced by the pressure to which they are subjected. Moreover, as the student will have observed in the preceding paragraphs, the atmospheric pressure modifies the boiling points of liquids to a marked extent.

The relation between the volume of a gas and the pressure acting upon it, is thus expressed—"The volume of a given weight of any gas is inversely as the pressure to which it is subjected." This law was enunciated, independently, by Boyle and Mariotte; and Dalton further showed that it was applicable to the case of a mixture of gases. The law, however, is not absolutely true, for the majority of gases increase disproportionately in density under high pressures; but, except under extraordinary pressures, or in the case of gases easily

* For a description of an ingenious instrument by Dr. Siemens, for measuring temperatures by means of electrical resistances, see *Journal of the Royal Institution*, 1871.

reduced to the liquid form, it may be assumed to be accurate for the purposes of ordinary calculation. By means of the apparatus represented in fig. 15, the differences in the rate of condensation of certain gases may be demonstrated. In the iron vessel, *v*, fits a rod, which can be depressed or raised by turning the handle, *C*; to the bottom of the vessel is attached an iron tube, *t*, leading to the massive block, *B*, in which are screwed two strong glass tubes, drawn out to a fine point at the upper end, and left open. The lower part of *v*, together with the tube, *t*, contains mercury; the upper portion of *v* is filled with oil. On screwing down the rod, the mercury is driven up into the tubes, so as to fill them completely. One of the tubes is then connected with a vessel containing dry ammonia, or sulphur-dioxide, or cyanogen,

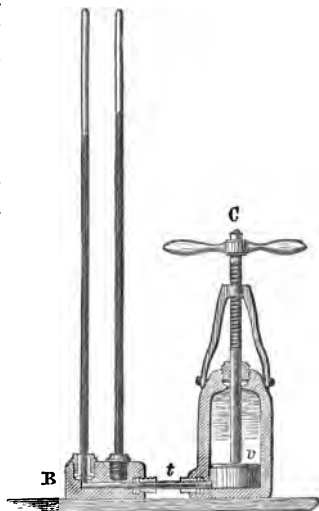


Fig. 15.

and the other with an arrangement for drying air. On raising the rod, the mercury falls simultaneously in the two tubes; the one thus becomes filled with dry air, the other with the dried gas, when the ends of the tubes are sealed off by means of the blowpipe. On again screwing down the rod, the mercury will be driven into the tubes, and the gases will be compressed. As the pressure is continually increased, the volume of the ammonia, if that gas be taken, is observed gradually to become less than that of the air; a given increment of pressure producing a greater amount of condensation in the ammonia than in the air; and, when the pressure amounts to about six or seven times that of the atmosphere, the disparity in the two volumes is rapidly increased, owing to the liquefaction of a portion of the ammonia. Even air itself, when

compared with hydrogen, suffers a greater contraction under a given increment of pressure. The following table shows the deviation of several gases from Boyle's law. It expresses the pressure, in metres of mercury, required to reduce the several gases originally under a pressure of 1 metre of mercury to $\frac{1}{2}$, $\frac{1}{3}$, &c., of their original volume. Carbon-dioxide, like ammonia, may be liquefied; hydrogen and air are permanent gases :—

Volume.	Air.	Carbon-dioxide.	Hydrogen.
	Metres.	Metres.	Metres.
1	1·000	1·000	1·000
$\frac{1}{2}$	4·9794	4·8288	5·0116
$\frac{1}{3}$	9·9162	9·2262	10·0560
$\frac{1}{4}$	14·8248	13·1869	15·1395
$\frac{1}{5}$	19·7198	16·7054	20·2687

19. The Barometer.—This instrument is made by completely filling with mercury a glass tube, sealed at one end, and of about 0·8 m. in length, and inverting it in a cistern containing the same metal. The mercury within the tube falls to a height of about 0·76 m. above the level of that in the trough (fig. 16). The most perfect forms of the instrument differ but slightly from this, which was the one originally devised by Torricelli. One of the main points in the construction of a barometer is to ensure that the space above the mercurial column (termed the Torricellian vacuum) is absolutely free from air, since this, by its tension, would counteract the atmospheric pressure, and cause the column to stand too low. In order to remove the last traces of air adhering to the mercury and glass tube, the metal requires to be heated to boiling. A very convenient method of boiling the mercury, and of obviating the risk of fracture in the tube, is represented in fig. 17. B is the barometer tube, perfectly clean and dry; it is connected by means of a thick and clean caoutchouc tube with the two-necked flask, A, containing the mercury; the neck, c, leads to an air-pump, or some other apparatus, by which A and B can together be exhausted. The mercury is heated to boiling in the vacuous flask, the tube

gently warmed by means of a lamp, and successive small portions of the heated mercury are now poured over into B, by inclining the flask, and again boiled, until the tube is completely filled.

As the barometric column rises and falls, the level of the mercury in the cistern alters; and, since the height of the column is always measured from this level, the scale must be movable, in order that its zero may be brought into adjustment. In practice, it is found more generally convenient to have the zero fixed as suggested by Horner, and to bring the level in the cistern into coincidence with it. This plan is adopted in the instrument represented in detail in fig. 18. The bottom of the reservoir consists of a piece of leather pressing against the rounded end of the screw, S; by raising or depressing this, the level of the mercury may be altered. Attached to the cover of the cistern is a small ivory point, *p*, with which the mercury can be brought into contact by means of the screw. When the point of *p* appears just to touch its image in the mercury the adjust-

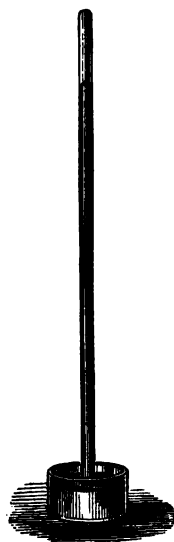


Fig. 16.

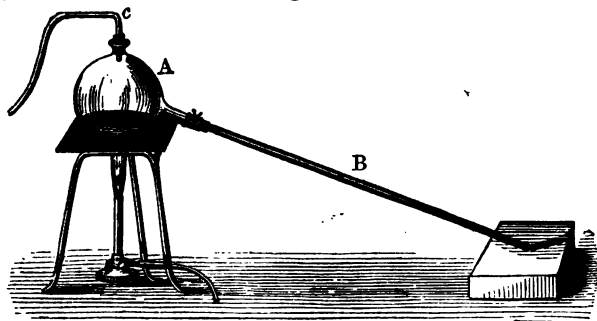


Fig. 17.

ment is complete. This point constitutes the zero of the

barometer scale. The tube is encased in a brass cover, in the upper portion of which two slits are made, to allow of the

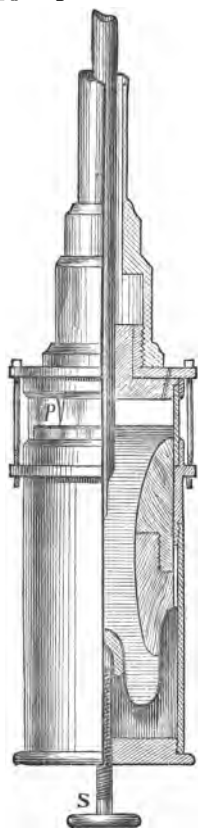


Fig. 18.



level of the mercury being read off on the attached scale. The reading off is facilitated by means of the little movable casing, *c c*, in which two slits are made coinciding with those in the brass envelope, but slightly wider, to allow the divisions on the latter to be easily seen. By the aid of a screw the upper interior edge, *e*, of the casing is made to coincide with the top of the meniscus of the mercurial column. Thus the height to the nearest millimetre is directly read off, the further subdivisions being determined by the nonius or vernier engraved on the movable casing.

When a very accurate measurement of the atmospheric pressure is required, a number of corrections have to be applied to the height of the mercurial column. The height of a barometric column (the at-

mospheric pressure being constant) varies inversely as the specific gravity of the liquid. The specific gravity of mercury at 4° is 13.596. Therefore the height of a column of water at 4°, corresponding to 0.76 m. of mercury, would be

$0.76 \text{ m.} \times \frac{13.596}{1.000} = 10.333 \text{ metres.}$ So also the column of pure alcohol (sp. gr. 0.80), corresponding to the same height of mercury, would be $0.76 \text{ m.} \times \frac{13.59}{0.8} = 12.916 \text{ metres.}$ But

the specific gravity of the mercury is not invariable; it diminishes with the temperature; on a hot day the barometric column will stand higher than on a cold day, when the atmospheric pressure is actually the same. In order, therefore, that its indications may be exactly comparable, it is necessary to correct for these deviations in specific gravity; or, in other words, to reduce the column of mercury to a uniform temperature, say to 0° . But the scale itself expands by heat, and contracts on cooling; it is only standard at 0° . This source of error to some extent counteracts that due to the variation in density of the mercury; but the indications of the scale require to be reduced to 0° in accurate measurements, from the known rate at which the material of the scale expands. In order to make these corrections, a small thermometer is attached to the barometer, to give the temperature of the scale and mercury.

The barometric column, if the tube is narrow, requires another slight correction for what is termed *capillary depression*. In a narrow tube the height of the mercury is invariably lower than in a wide tube. The depression is due to the fact that the particles of the metal are attracted much more strongly to each other than to the glass. The error arising from this depression may be calculated when the diameter of the tube is known. But this and other errors, due to slight impurities in the mercury, air in the tube, imperfect division of the scales, &c., are conveniently merged into one correction by comparison with a standard instrument.

20. Expansion of Gases by Heat.—If we simultaneously heat a rod of iron and a rod of copper of equal lengths, through the same interval of temperature, say from 0° to 100° , we notice that the copper lengthens more than the iron.

If we partially fill two thermometer tubes of equal capacity with the same volumes of mercury and water at 0° , and

heat the tubes to 100° , the volumes of the liquids at the higher temperature will be also different; if we call the volumes at 0° 1,000, the volume of the water at 100° will be 1,043, and that of the mercury 1,018.

Moreover, if we compare the rate of expansion of one of the solid substances between 0° — 100° with the rate between 200° — 300° , we notice that the increment of 100° at the higher temperature produces a greater expansion than the same increment between the lower interval. This is even more marked in the case of liquids. 100,000,000 cub. m.m. of mercury, measured at 0° , become 100,017,905 cub. m.m. at 1° ; whereas 100,000,000 cub. m.m., at 300° , become 100,019,413 cub. m.m., at 301° .

But, if we empty the thermometer tubes and dry them perfectly, and fill one with coal gas, leaving the other filled with air, and introduce into the stem of each a short column of mercury to serve as an index, so arranging matters that the positions of the indices are identical (showing that the same volumes of air and coal gas are confined in the tubes), and then heat them both through the same interval of temperature, say from 0° — 100° , we notice that the air and gas expand at precisely the same rate; both occupy the same final volume. If we call the volume of each at 0° 1,000, the volume of both at 100° will be 1366.5. Hydrogen, oxygen, carbon-dioxide, or indeed any other gas, might have been taken to compare with air; the result would have been the same. If, moreover, we compare the expansion of a gas between two intervals, we find that its rate is identical. These facts may be thus expressed:—*The volume of a gas under constant pressure expands when heated by the same fraction of itself, whatever be the nature of the gas.* This law was discovered by Charles, but was first properly verified by Gay-Lussac.

As the constant expressing the rate of expansion of a gas is of frequent use in chemical calculations, it may be desirable to describe the methods by which it was obtained. Fig. 19 represents the apparatus employed by Gay-Lussac. A glass tube, about 30 c.m. long and 1 m.m. wide, has one end blown out into a bulb of 1 c.m. in diameter. The tube is graduated and the capacity of the bulb determined in

terms of one division of the scale—that is, the weight of mercury contained within the space 0—1 of the scale is divided into the weight contained in the bulb and portion of the tube up to the zero. The bulb and tube are filled with dry air and placed in the vessel, B, as represented in the figure. The instrument is then surrounded with melting ice, when the air within contracts; the amount of this contraction is ascertained from the movement of a short column of mercury contained within the

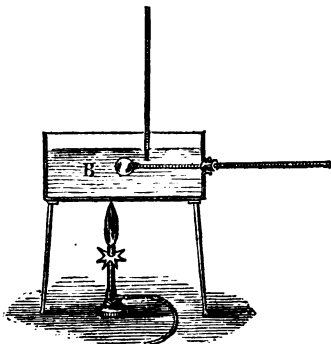


Fig. 19.

tube. When the column is stationary, its position is read off on the graduated scale. We have thus a determinate volume of air at 0° within the tube. The ice is now replaced by hot water, the temperature of which is determined by a thermometer; and the expansion of the confined air, as indicated by the movement of the index, is compared with the readings of the thermometer. The immediate results of the experiments require several corrections, especially one for the change in the capacity of the glass envelope, since this, like the air, expands on being heated. After eliminating all known sources of error, Gay-Lussac found that 1,000 volumes of dry air, at 0° , become 1,375 volumes at 100° .

Subsequent experiments, made by a more refined method, have shown that this result is slightly too high. From the investigations of Regnault and Magnus, it appears that 1,000 volumes of dry air, at 0° , become 1366.5 volumes at 100° ; or 1 volume, at 0° , becomes 1.003665 at 1° . This fraction of increase for 1° (which may also be represented as $\frac{1}{273.15}$, or $\frac{1}{273}$) is called the *coefficient of expansion for air*. The very accurate researches of Regnault have further proved that the degree of expansion increases with the pressure: thus, under a constant pressure of .110 m., it is 1.003648; under a pressure of 3.653 m., it is 1.003709. Moreover, it appears that

each gas has its particular coefficient of expansion—the gases most easily condensed to the liquid form expanding to the greatest extent between 0° and 100° :—

1 volume of hydrogen, at 0° ,	becomes	1.36613	volumes at 100° .
„ carbon-dioxide, „		1.37099	„
„ cyanogen, „		1.38767	„
„ sulphur-dioxide, „		1.39028	„

The student will bear in mind that similar deviations from the law of Boyle and Mariotte are exhibited by these gases. For the purposes of calculation, we may assume that the coefficients are practically equal—viz., that all gases on being heated expand $\frac{1}{273}$ part of their volume at 0° C. for 1° C.

Since gases are affected so greatly in volume by changes of temperature and pressure, it is requisite, in comparing the weights of equal bulks, to have a standard of temperature and pressure. By common consent it has been agreed to take 0° as the standard point of temperature, and 0.76 m. (the mean height of the barometer at the sea's level in the latitude of Paris) as the standard of pressure.

21. Density of Gases.—As the weights of the various gases are their most characteristic physical constants, it is desirable that we should now explain the method by which these weights have been experimentally ascertained. The most refined method is due to Regnault, who has determined, with the greatest possible accuracy, the absolute weight of the more important gases. The principle of this method is extremely simple. A vessel of known capacity was weighed when vacuous and when filled with the gas under investigation at a definite temperature and pressure. The difference between the weighings expressed the weight of a determinate volume of the gas. A glass balloon (A), of about 10 litres capacity, was fitted with a stop-cock, and its volume and the amount of air it displaced were determined—(1.) By weighing it filled with water in the ordinary manner; and then (2.) by weighing it, still filled with water, in water of the same temperature. The difference between the two weighings gave the weight of the water displaced by the external volume of the balloon. A similar sized glass globe (B), of the same kind of glass and of nearly equal weight, was fitted with a cock and hook, and the volume displaced by it also ascertained. If less than

that of A, its volume was equalized by hanging a glass tube sealed at both ends, on its hook, so that the volume of air displaced by the two globes was equal. By using globe B

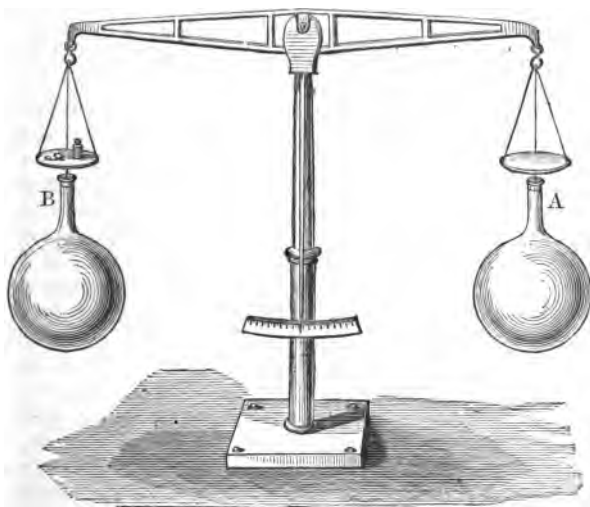


Fig. 20.

as a counterpoise to globe A, all correction for the volume of air displaced by the globe in which the gases are weighed is obviated; as the same weight of air is displaced on each side of the balance, the ratios of the weights remain unaltered, the weighings are thus rendered independent of any variations in the temperature, pressure, and in the hygrometric condition of the atmosphere. (Fig. 20). The balloon A was then connected with a three-way tube, so that it could be put in connection at will either with a reservoir of gas, or an air-pump and manometer. (Fig. 21). The balloon

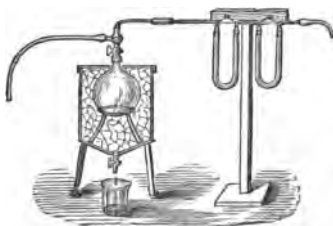


Fig. 21.

was now exhausted as completely as possible, and the gas allowed to enter from the gas-holder in a slow stream, so as to insure its complete desiccation as it passes through the U-tubes filled with pieces of pumice, moistened with concentrated sulphuric acid. The balloon was again exhausted, and again filled with the dry gas, the process of exhaustion and re-filling being repeated until the amount of air left in the vessel was inappreciable. Before the balloon was filled for the last time, it was surrounded with ice in the manner shown in the figure. By momentarily opening the cock, before the balloon was withdrawn from the ice, the gas acquired the tension equivalent to the atmospheric pressure at the moment. This was ascertained from the height of the barometer. The globe was now carefully wiped by a damp cloth (to prevent electrical excitation, which would affect the weighings), and hung, together with the counterpoising balloon, upon the balance. As soon as the vessels had acquired the temperature of the balance-case, their difference in weight was carefully ascertained. The balloon was removed from the case and again surrounded by ice, and the gas withdrawn by the air-pump as far as practicable, the tension of the residual gas being determined from the height of the mercury in the manometer. The globe was again suspended from the balance, and weighed with the same precautions as before. The difference between the weighings ($W - w$) gives the weight of the gas filling the balloon at 0° under the atmosphere pressure H , diminished by the tension h of the residual gas. The weight of the gas at the standard temperature and pressure is, therefore, $(W - w) \frac{760}{H - h}$.

The following table gives the weight of 1 litre of some of the more important simple gases at the standard temperature and pressure :—

GAS.	Symbol.	Weight in Grams.	Density. $H = 1$.	Combining Weight.
Hydrogen,.....	H	0.0896	1	1
Oxygen,.....	O	1.4298	16	16
Nitrogen,.....	N	1.2550	14	14

If the observed density of hydrogen be called 1, the densities of the other gases become raised to the numbers contained in the fourth column. Now, if these be compared with the numbers contained in the fifth column, which express the combining weights of the respective gases obtained from the table on p. 17, a very striking relation at once appears. *The densities of the elementary gases are identical with their combining weights, when hydrogen is taken as the unit both of weight and density.* (Compare p. 17). It is evident, therefore, that a given volume of any two gases at the same temperature and pressure must contain the same number of molecules.

CHAPTER III.

22. Hydrogen.—Symbol H. Atomic weight 1. Density 1.

This body occurs very sparingly distributed in the free state on the earth. It is contained in the human breath under certain conditions. Certain volcanic exhalations contain as much as 25 per cent. by volume of this gas ; it is also found to accompany the remarkable jets of steam known as *fuimerolles*, which occur in various parts of the world, particularly in Tuscany. Hydrogen is *occluded* in variable amount in many meteorites, and it is held to be a distinguishing characteristic of these bodies. But all terrestrial sources of free hydrogen are utterly insignificant when compared with the enormous reservoir of this gas which exists around the sun. Spectroscopic investigations have proved to us that it is one of the chief constituents of the gaseous envelope of our great luminary.

In a state of combination hydrogen is very abundant on the earth. It forms one-ninth of the weight of water, and one-fourth of the weight of marsh-gas, a gas largely exhaled from many subterranean sources ; it constitutes a

large proportion of the bodies of animals and plants, and indeed is an essential constituent of nearly all organic compounds. It is, moreover, an essential element in the extensive class of bodies termed *acids*.

23. Its Preparation.—The evolution of an inflammable gas, during the solution of iron in dilute sulphuric acid, appears to have been observed in the sixteenth century by Paracelsus ; but the first exact study of the nature of this gas was made by Cavendish in 1766 ; he established its individuality, and termed it *inflammable air*. He showed that other metals than iron—viz., zinc and tin—when acted upon by sulphuric and hydrochloric acids, evolve this air in amount varying with the nature of the metal.

This method of obtaining hydrogen is still the one most commonly practised ; the apparatus represented in fig. 22

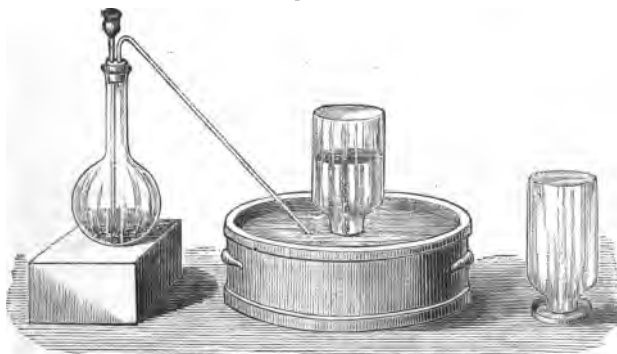
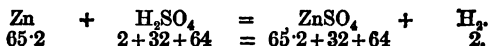


Fig. 22.

serves for the preparation of the gas. The flask contains fragments of zinc covered with a little water ; below the surface of the liquid dips the end of the funnel tube, through which the dilute sulphuric acid is poured. An energetic effervescence is set up as the zinc dissolves, and, so soon as the air within the apparatus is expelled, pure hydrogen is disengaged in bubbles from the tube ending beneath the water in the trough. If a bottle filled with water be inverted beneath the surface of the liquid in the trough, and held over the stream of gas, the water will be gradually

displaced as the bottle is filled with hydrogen. The end of the tube dips beneath a hole in a little shelf or stand on which the bottle to be filled is placed. This very simple and convenient arrangement for collecting gases was devised by Dr. Priestley : it is called the *pneumatic trough*.

The equation representing the action of sulphuric acid upon zinc is—



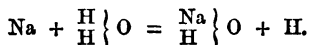
which indicates that 65.2 grams of zinc, when acted upon by 98 grams of sulphuric acid, yield 2 grams of hydrogen, and 161.2 grams of zinc sulphate. The zinc sulphate remains in solution in the flask ; it may be obtained by concentrating the liquid sufficiently, when the salt crystallizes out.

The evolution of the hydrogen is modified in a remarkable manner when the substances react upon each other under pressure. If the zinc and sulphuric acid, in the proportion indicated by the above equation, be brought together in a sealed tube—that is, under such conditions that the evolved hydrogen, being confined, exerts a considerable pressure upon the reacting substances—it is noticed that, long before the whole of the metal is dissolved, all action ceases. This diminution of chemical action is regarded by some, not as a direct consequence of increased pressure, but as due to the creation of a layer of saturated solution of zinc sulphate upon the surface of the metal ; owing to the diminished size of the gas-bubbles under the pressure, the removal of this layer is retarded, whereby the zinc is protected from the action of the acid. There are, however, other cases of diminution in chemical action under great pressure which do not appear to admit of such simple explanation.

If iron be substituted for zinc in the preparation of hydrogen by the foregoing method, the gas almost invariably acquires a peculiar and disagreeable odour, owing to the presence of small quantities of compounds of carbon and hydrogen. Iron, especially cast-iron, contains carbon, which, in presence of the hydrogen evolved on dissolving the metal, is in part converted into hydrocarbons of the C_nH_{2n} series (C_2H_4 ,..... C_6H_{12}).

We have already stated that hydrogen is a constituent of water; many methods have been devised for freeing it from its combination. One of the simplest consists in throwing a piece of sodium or potassium into the water, when the liquid is immediately decomposed; these metals, being specifically lighter, float upon the surface of the water, and, in the case of the potassium, the heat developed is so great that the hydrogen in contact with the air inflames and burns with a bright *violet* light, owing to the presence of a little vapour of potassium. Under ordinary circumstances the hydrogen evolved from water by sodium does not take fire; if, however, the water be warmed, or if the free motion of the sodium be impeded as it rolls over the surface by increasing the viscosity of the liquid with gum or starch solutions, the hydrogen inflames and burns with a *yellow* flame, due to the presence in it of a trace of volatilized sodium. By filling a tube with water, inverting it in the trough, and quickly bringing into it a small piece of the sodium, the hydrogen evolved may be collected.

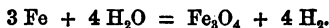
Water is a combination of 2 parts by weight of hydrogen united to 16 parts of oxygen; the chemical symbol of water is H_2O . The sodium turns out half the hydrogen in the water, and takes its place, forming a caustic alkaline substance termed *sodium hydroxide*. Thus—



This equation implies that 23 parts of sodium liberate 1 part of hydrogen from water and form 40 parts of sodium hydroxide. If K be substituted for Na in the above equation, it would mean that 39.1 parts of potassium liberate 1 part of hydrogen, and produce 56.1 parts of potassium hydroxide. The presence of the hydroxide may be detected in the solution either by its caustic taste or by its action on certain vegetable colouring matters—*e. g.*, a solution of litmus, reddened by a drop of acid, which will immediately be turned to a blue colour; if an infusion of purple cabbage be substituted for the reddened litmus, the colour will be changed to green.

Many metals have the power of decomposing water at a high temperature, combining with the oxygen and liberating

the hydrogen. Thus, when the vapour of water is passed over red hot iron, hydrogen is produced, together with an oxide of iron, known as *triferric tetroxide*—



In this reaction it will be observed that the whole of the hydrogen is evolved, none remaining in combination with the oxide.

Certain metals, such as platinum, are unable to effect the decomposition of water at any temperature. If, however, the platinum be brought into intimate connection with zinc or magnesium, the combination will decompose water at the ordinary temperature without the intervention of an acid. Copper also, which requires a very high temperature to bring about the decomposition of water, when deposited on zinc, effects its decomposition slowly at the ordinary temperature, but rapidly if the water be gently heated. If a few grams of zinc-foil are plunged into a dilute solution of copper sulphate, the copper will be deposited on the zinc. If, when the surface of the zinc is well covered with spongy copper, the metals are withdrawn and thoroughly washed with distilled water, and immersed in a flask filled with pure water, hydrogen will quickly appear in small bubbles on the surface of the copper, and zinc oxide will be formed. If the liquid be heated to the boiling point, the disengagement of the hydrogen will be rapidly increased, and the gas may be collected over the trough in the ordinary manner.*

24. Its Properties.—Hydrogen, when perfectly pure, is a colourless invisible gas without taste or smell. Even when exposed to a pressure of 3,000 atmospheres it still retains its gaseous condition. It is very slightly soluble in water; 100 c.c. of water dissolve 1.93 c.c. of the gas. It is worthy of remark that the degree of solubility is unaffected by the temperature of the liquid. The lower animals are instantly suffocated when immersed in the gas; but when mixed with air it may be breathed for some time by man with impunity, as it has no toxic action; when inhaled in sufficient quantity, it gives a peculiar squeaking tone to the voice, by reason of its

* Gladstone and Tribe, *Proc. R. S.*, 133, 218, 1872.

extreme tenuity. Hydrogen is inflammable, and burns in the air with a very feebly coloured flame; usually its colour is slightly blue, an effect said to be due to the presence of minute traces of sulphur, either in the gas itself, and derived from its mode of preparation, or in the air in which it burns. In the act of burning in the air it combines with oxygen to form water—a fact first noticed, although not explained, by Macquer, in 1766. Hence the name given to the gas—from *ὕδωρ*, *water*; and *γεννάω*, *I produce*.

The production of water from burning hydrogen may be

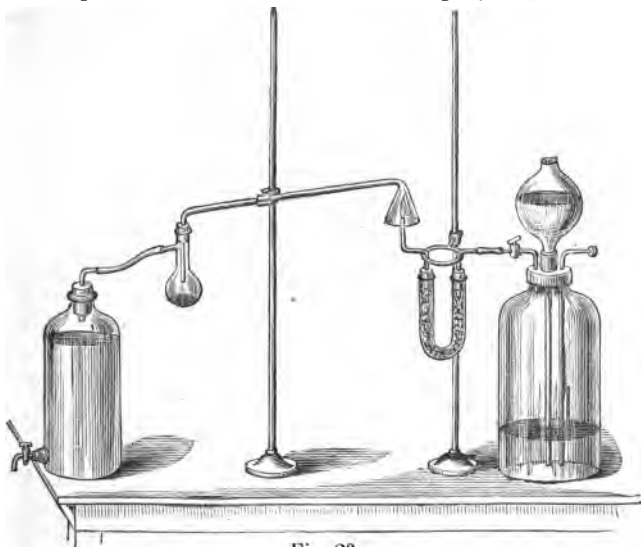


Fig. 23.

demonstrated by means of the apparatus seen in fig. 23. Hydrogen is delivered from the gas-holder, and traverses the U tube, filled with calcium chloride, to absorb any aqueous vapour which it may contain. The dry gas is burned beneath the funnel, connected with a glass tube about 70 c.m. long and 1 c.m. wide, ending in the little receiver, the side tube of which is connected with the large bottle filled with

water, which acts as an aspirator; the flow of water may be regulated by the stop-cock. As the heat of the flame would speedily fuse the edges of the glass jet together, an extemporized jet of platinum, made by tightly rolling a small piece of foil round a thick pin, is inserted into the glass jet. The edges of the glass tube may, if necessary, be fused to the platinum by momentarily holding the tube in the Bunsen gas flame. By means of this apparatus, in about thirty minutes, 15 or 16 c.c. of water may be condensed in the receiver from 20 litres of hydrogen.

Substances burning in the air are immediately extinguished on being plunged into an atmosphere of hydrogen: thus a lighted taper, pushed into a vessel filled with the gas and held mouth downwards, sets fire to the hydrogen, but is itself extinguished. When mixed with air in certain proportions, this gas forms an explosive mixture; the loudest detonation is given with a mixture of 1 volume of hydrogen and $2\frac{1}{2}$ volumes of air. That it is the oxygen in the air which, in the act of combination with the hydrogen, produces this explosion, may be shown by inflaming a mixture of 1 volume of hydrogen and $\frac{1}{2}$ a volume of oxygen, equal to that contained in $2\frac{1}{2}$ volumes of air, when a similar but more energetic explosion will result. The increased force of the explosion, in the latter case, is due to the absence of the nitrogen, which, in the case of the air, acts as a diluent. Great care must be taken, in experimenting with the gas, to insure that it is free from admixed air; before collecting it over the trough, a considerable amount should be allowed to escape from the apparatus, so as to be certain that the last traces of air have been expelled. The operator may assure himself of its freedom from air by collecting a small quantity of the issuing gas in a test tube, and bringing it, mouth downwards, in contact with a flame: if the hydrogen contains air in any quantity, it will detonate; if sufficiently pure to be collected, it will burn quietly.

Hydrogen is the lightest body known. It is 14.47 times lighter than air; it may therefore be poured upwards. If a jar filled with the gas be brought, mouth downwards, in contact with the mouth of a similar jar or beaker, also inverted but filled with air, and the former jar be gradually turned

mouth upwards, the hydrogen will pass out into the upper vessel, and displace the air it contains. (Fig. 24). The presence



Fig. 24.

of the hydrogen in the upper vessel may be ascertained by bringing a lighted taper to its mouth; its absence in the lower one may be rendered evident by pushing the taper within the vessel, when the flame will continue to burn quietly. On account of its great levity, hydrogen was formerly employed for aërostatic purposes, but its use has now been almost entirely superseded by that of coal gas.

25. The Crith.—One litre of dry hydrogen at the standard temperature and pressure weighs 0.0896 gram. This number is of very frequent use in chemical calculation; it is the coefficient by which the weight of 1 litre of any other gas, simple or compound, may be calculated. To denote this constant, the term *crith* (from κριθή, a barley-corn) has been suggested.

26. Gaseous Diffusion.—An open bottle, filled with hydrogen, may be held mouth downwards for a short time without any perceptible quantity of the gas mixing with the air. In time, however, the hydrogen, in spite of its lightness, will be

found to have escaped from the bottle, and its place will be occupied by air, which is 14.47 times heavier. Thus, from an inverted bottle of 1,000 c.c. capacity, 816 c.c. of hydrogen escaped in four hours, and 945 c.c. in ten hours, its place being supplied by an equal volume of air. The fact that two gases will mix with each other, despite their difference in density, may be illustrated in a variety of ways. If a flask containing hydrogen be connected with one containing carbon dioxide, which is twenty-two times heavier, in the manner seen in fig. 25, the hydrogen being at the top, and the carbon dioxide at the bottom, after a certain interval of time, half of the heavier carbon dioxide will be found in the upper flask, whilst half of the hydrogen will be found in the lower one; in other words, the one gas makes its way from vessel to vessel, as if the other were absent. This fact Dalton expressed by saying, that *one gas acts as a vacuum towards another*; for what is true of hydrogen and carbon dioxide is true of all gases which are without chemical action on one another.

When two or more gases have thus diffused themselves uniformly through one another, they never separate again in the order of their specific gravities.

Paradoxical as it may appear, the rapidity with which a gas lighter than air makes its escape from an inverted bottle is in proportion to its levity. *The lighter it is the more quickly does it diffuse.* Experiment shows that *the diffusibility of two gases varies in the inverse ratio of the square roots of their densities.*

Two bottles of 100 c.c. capacity were filled respectively with hydrogen and carbon dioxide, and so arranged that the bottle of hydrogen was mouth downwards, whilst that of carbon dioxide was upwards; it was found that 47 c.c. of hydrogen escaped in two hours, whilst it required ten hours for the same volume of carbon dioxide to diffuse. The proportion of 1 : 5 is very nearly as that of the square root of the density of

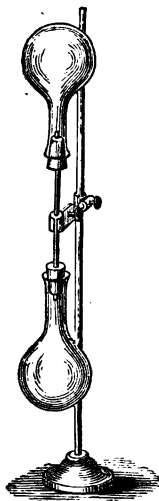


Fig. 23.

hydrogen, 1, to the square root of the density of carbon dioxide, 22.

The intra-diffusion of gases takes place even through very small pores: the ratios of their diffusibilities are not altered by varying the magnitude of the connecting apertures. It has been observed that hydrogen diffuses out of a cracked jar standing over the pneumatic trough with such rapidity that the water rises within the jar, an equal volume of air not being able to enter the jar through the crack at the same rate. By means of the *diffusimeter* the rapidity of this interchange may be more easily rendered evident. This instrument consists of a glass tube of 2 or 3 c.m. in diameter, and 25 c.m. in length, open at one end, and closed at the other by a diaphragm of some porous material. The material originally

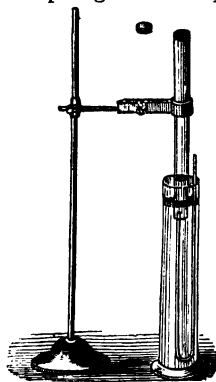


Fig. 26.

employed by Graham, by whom the phenomena of gaseous diffusion were investigated, was gypsum. A closely fitting cylinder of wood was pushed into the tube to within about 5 m.m. from the end, the unoccupied space being filled with gypsum paste of the consistency usually employed for taking casts. When the plug was sufficiently hardened, the wooden rod was withdrawn; and by allowing the stucco plate to dry by exposure to the air it became permeable to gases. Various other materials may be used for the diaphragm—*e. g.*, paper, charcoal, wood, dry bladder, cork, &c., but probably the most advantageous substance is artificially compressed graphite, which may be obtained in thin discs, like wafers, not exceeding half a millimetre in thickness; these may be readily cemented on to the end of the tube. A plug of unglazed earthenware or biscuit may also be substituted for the stucco. When the diffusimeter is to be used, the diaphragm is covered with a piece of unvulcanized caoutchouc, and the tube is filled with mercury; if water be used, it must not touch the septum, or its action will be arrested; in such a case, the shorter limb of a syphon is introduced into the diffusimeter

to within 1 c.m. or so of the stucco, and the air displaced by sinking the tube in the trough; the syphon is withdrawn, and the tube filled with the gas. On removing the caoutchouc cover, the gas diffuses through the pores of the diaphragm, and, in the case of hydrogen, with such rapidity that the water rises several inches within the tube. (Fig. 26). The specific gravities of hydrogen and air being respectively 1 and 14.47, their diffusibilities will be in the ratio of $\sqrt{14.47}$ to 1; that is, for every 3.8 c.c. of hydrogen escaping from the tube, 1 c.c. of air enters in its place.

This fact may be admirably illustrated by means of the apparatus seen in fig. 27. The glass tube, *a*, is about 1 metre in length, and 1 c.m. in diameter; it is fixed into the porous cell, *b* (such as is employed in galvanic batteries), by means of a well-fitting india-rubber cork. The other end dips into the vessel filled with water, coloured by a few drops of indigo solution, in order to render its movement more perceptible. If a jar of hydrogen be brought over the cell, this gas will enter through its pores much more quickly than the air within can make its way out; the excess of pressure within the apparatus causes a portion of the mixed gas and air to escape in bubbles from the end of the tube in the water. As, from the arrangement of the apparatus, the mixed gas cannot escape, it presses upon the surface of the water in the two-necked flask, and drives it out through

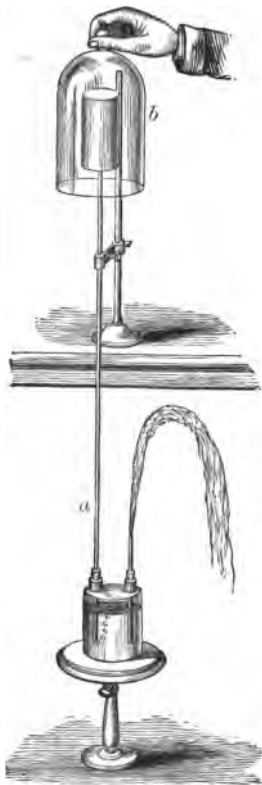


Fig. 27.

the narrow jet. As soon as the jar is removed, the hydrogen commences to diffuse out of the cylinder with much greater rapidity than the air can enter in its place, so that a partial vacuum is created within the apparatus, and the coloured water is driven up the glass tube.

The following table shows the rates of diffusion of several gases, simple and compound, as determined by Graham. The density of the gases in column I. is compared with air as unity; column II. gives the inverse square roots of these densities; and column III., the observed velocity of diffusion.

GAS.	I.	II.	III.
Hydrogen,.....	0·06926	3·779	3·83
Nitrogen,	0·9713	1·015	1·014
Oxygen,	1·1056	0·951	0·949
Carbon dioxide,.	1·5290	0·809	0·812

Graham has further shown that hydrogen penetrates through a porous septum into a vacuum with the same absolute velocity as into air, thus establishing the fact that the force promoting diffusion is identical in both cases. It is only when the diaphragm is very thin that gases diffuse in this ratio; if it is thicker, so that it may be assumed to consist of a series of capillary tubes of great length in proportion to their diameter, the passage of the gases occurs at very different rates. The movement of gases through very narrow tubes (called capillary transpiration) is regulated by other laws than those governing gaseous diffusion.

27. Atmolysis.—Advantage may be taken of the varying diffusibilities of gases to effect a partial separation of the constituents of a gaseous mixture. Such a process of separation by diffusion is termed *atmolysis* (from ἀτμός, *gas*; λύω, *to loosen*). If a mixture of oxygen and hydrogen, in the proportion to form a detonating gas, be allowed to flow slowly through a stucco tube (a clay tobacco pipe does very well), the end of which dips under the shelf of the pneumatic trough, the hydrogen will diffuse through the pores of the pipe with so much greater rapidity than the oxygen, that the issuing gas collected in the tube no longer detonates on the approach

of a light, but, on account of the increased proportion of oxygen it contains, supports combustion with increased vigour (fig. 28). This process affords a method of deter-

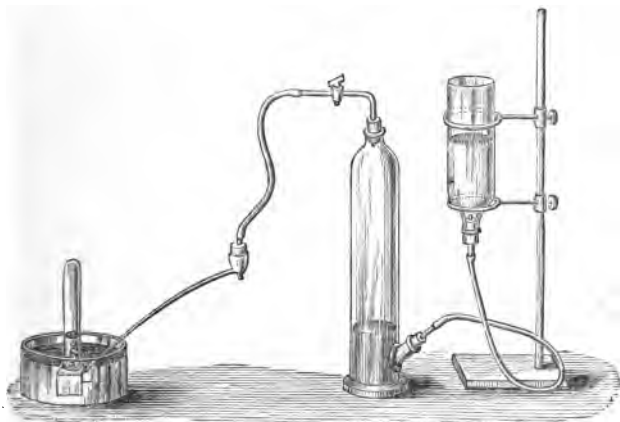


Fig. 28.

mining whether a certain gas is a mixture or an individual: if the results of its analysis, before and after atmolysis, are identical, we may conclude that the gas is not a mixture.

28. Constitution of Gases.—The investigation of these remarkable intestinal movements of gases has conduced, together with other considerations which cannot here be entered into, to the adoption of a theory of the constitution of gases which connects together all their laws which we have hitherto studied. According to this hypothesis, a gas consists of an aggregation of molecules moving incessantly and with great rapidity. The rate of movement of the particles is variable by reason of their ceaseless mutual encounters; at the same instant some are moving rapidly, others slowly, whilst the greater number move with an intermediate velocity. To this incessant movement of their constituent molecules, is due the principal characteristic of gases, viz., their elasticity or expansive tendency. The outward pressure which they exert on any containing surface is the aggregate effect of the impact of their molecules: it is

proportional to the sum of the masses of the molecules multiplied into the squares of their velocities. If we halve the containing space, we double the number of impacts in a given time—that is, the number of impacts in a given time varies inversely as the volume of gas; this is equivalent to saying that the pressure exerted by a gas varies inversely as its volume, which is nothing else than the law of Boyle and Mariotte.

We have already stated that the number of molecules in the unit volume of any gas, whatever be its nature, is the same whilst their masses are variable; and this law admits of independent demonstration by the aid of the dynamical theory of gases. It follows therefore that the mean velocities of the molecules of different gases must be variable. It has been calculated that at 0° C. the mean rapidity of the molecules of—

Hydrogen	is	1,844	metres	per	second.
Oxygen	"	461	"	"	"
Nitrogen	"	492	"	"	"

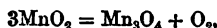
These numbers accord with those demanded by the law of the diffusion of gases, which states that the rate at which a gas is translated is in the inverse ratio of the square root of its density. The density of hydrogen being 1, that of oxygen is 16, and $\sqrt{16} = 4$; the ratio of 4 to 1 is as 1,844 to 461.

29. Oxygen.—Symbol O; atomic weight 16; density 16.

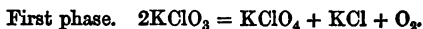
Oxygen is the most widely diffused of all the elements. It occurs in the free state in the air, of which it forms nearly one-fifth by volume; in combination it constitutes nearly half of the mass of the earth; it forms about eight-ninths of the weight of water; and it is an essential constituent of all organisms.

30. Its Preparation.—Oxygen was discovered by Priestley in 1774. He obtained it by heating mercuric oxide which, as we have already learned, yields nearly 8 per cent. of its weight of the gas. The Swedish chemist Scheele discovered it, independently of Priestley, in 1775, and termed it *empyreal air*, from its characteristic power of supporting combustion.

Many other combinations of oxygen and metals may be used as sources of the gas, some of which, like mercuric oxide, yield the whole of their oxygen, whilst others part with only a definite proportion of it. Manganese dioxide may be taken as an example of the latter class; when heated, it is decomposed in accordance with the reaction—



manganese dioxide yielding oxygen and trimanganic tetroxide. This method of preparing the gas is occasionally employed in the laboratory. Oxygen is an essential constituent of many saline substances, such as nitre, potassium chlorate, &c. The latter substance indeed constitutes the general source of oxygen in the laboratory. When potassium chlorate is heated to about 370° it melts, and at about 400° it commences to evolve oxygen gas, which is rendered evident by the appearance of effervescence in the molten mass. After a time the salt partially solidifies, and if the heat be continued to low redness, the mass becomes suddenly incandescent, and evolves a further quantity of oxygen. The decomposition of potassium chlorate evidently occurs in two phases. The first action of heat converts the salt into potassium perchlorate, potassium chloride, and oxygen—



And on increasing the heat, the potassium perchlorate is decomposed into potassium chloride and oxygen—



The temperature required to expel the total amount of oxygen contained in potassium chlorate is therefore very high. The difficulty of obtaining the whole of the oxygen is increased by the circumstance that the partial solidification of the salt occurs soonest near the sides of the vessel, which thus become lined with a mass of badly conducting material, whereby the decomposition of the salt in the interior is retarded. If the decomposition is effected in glass flasks, these, at the high temperature needed, become softened, and lose their shape.

If, however, the potassium chlorate, in a state of powder, is mixed with certain finely divided substances, which exert

no chemical action upon it, the salt never fuses on heating, and the complete expulsion of the oxygen occurs at a much



Fig. 29.

lower temperature. The substances which most readily promote the decomposition of the salt are cupric oxide, manganese dioxide, and ferric oxide. If an intimate mixture of 4 parts of finely powdered potassium chlorate, and 1 part of cupric oxide, obtained by precipitation,

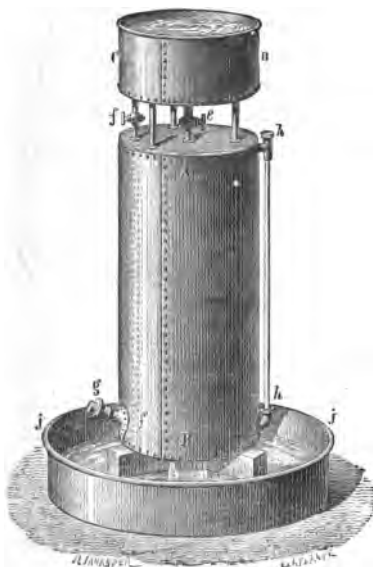


Fig. 30.

be heated, oxygen begins to be evolved at about 250° , and at about 300° the decomposition is very rapid. At a few degrees higher, the mass suddenly becomes heated, solely from the energy of the decomposition, and its temperature rises to nearly 400° , when the remainder of the oxygen is instantaneously evolved. The whole of the salt is converted directly into potassium chloride without the copper oxide suffering the slightest change. Similar results are obtained by substituting either of the other oxides; with ferric oxide, however, the total decomposition of the salt requires a longer time; in neither case is the

oxide in any degree modified. The decomposition in all

cases is accelerated when the substances are fully powdered and intimately mixed. By carefully regulating the heat, the temperature may be maintained at about 300° when the evolution of gas is uniform and regular: if the temperature be allowed to exceed this point, so that the decomposition becomes violent, a small quantity of chlorine is simultaneously evolved. The apparatus seen in fig. 29 serves for the preparation of oxygen by this method: the mixture of potassium chlorate and manganese dioxide is heated in the small flask fitted with a cork and bent delivery tube; as soon as the gas commences to come over rapidly, it may be collected in the bottles filled with water and standing inverted on the shelf.

31. Storage of Gases.—Large quantities of the gas may be conveniently stored in the gasometer, represented in fig. 30. AB is a cylinder of sheet zinc or copper, surmounted by a cistern, CD; at *f* is a tube (provided with a stopcock) which connects the cylinder and cistern, and reaches very nearly to the bottom of the former. On allowing water to flow down this tube from the cistern, the air or gas within the cylinder is expelled through the tube *e*, which is also fitted with a stopcock; at *g* is a lateral tube placed at an acute angle with the cylinder, which can be closed by a screw cover fitting into its mouth. In order to fill the apparatus with gas (say with oxygen), the two stopcocks are opened, and water poured into the cistern until the cylinder is filled; the two stopcocks are then closed and the cover of *g* unscrewed; the mass of water in AB is prevented by the atmospheric pressure from flowing out. The delivery tube of the apparatus furnishing the oxygen is then pushed through *g* into the cylinder; as the gas is evolved, it displaces the water, which flows out past the tube into the trough, *j j*. The amount of gas in the cylinder is seen from the height of the water-level in the gauge, *h h*. When it is necessary to fill a vessel with oxygen from the store in the cylinder, water is poured into the cistern, and the vessel, also filled with water, is brought over the tube *e*, the stopcocks *e* and *f* are then opened, water flows down *f* and drives the gas through *e*, which displaces the water in the vessel. As soon as the vessel is filled the cocks *e* and *f* are shut. Instead of sending the gas through *e*, it may be expelled through a short side tube on the top of the cylinder (not shown in the figure)

furnished with a stopcock ; by attaching a caoutchouc tube to the end, the gas may be led to any desired position.

32. Action of the Admixed Oxides on the Potassium Chlorate.—It must be carefully borne in mind that, so far as we at present know, the oxides promoting the decomposition of the potassium chlorate are in nowise altered during the process. It might be supposed, from the fact of their containing oxygen, that they contributed to the amount of gas evolved. Manganese dioxide, it is true, as we have already mentioned, parts with a portion of its oxygen when heated ; but the temperature of its decomposition is far higher than that at which even the unmixed potassium chlorate is decomposed. We shall have occasion to observe many other instances in which a body promotes or initiates the decomposition of a substance, or resolves it into another substance apparently by its mere presence, and without itself suffering change. Such phenomena are referred to under the term *catalysis* : the manganese dioxide, and the cupric and ferric oxides are, with reference to the above reaction, called *catalytic agents*. It is very difficult to give an explanation of catalytic action to cover all the observed cases. Some may be explained on the assumption, that the body in contact exerts an amount of affinity, sufficient to upset the equilibrium of the substance to be decomposed, but that under the conditions of the decomposition this affinity cannot possibly be satisfied. The effect of heat upon potassium chlorate is to loosen the affinities of the oxygen atoms for the potassium and chlorine ; when the salt is in intimate contact with a substance like manganese dioxide, which exerts an affinity for oxygen by its tendency to pass into a higher state of oxidation, the force tending to decompose the substance is augmented ; it is made up of the loosening effect of heat *plus* the affinity exerted by the manganese dioxide. But at the temperature of decomposition the higher oxide cannot permanently exist ; supposing it to be formed, it would instantly be decomposed. A similar case of catalytic action is seen in the action of nitric and oxalic acid upon one another. Their mutual decomposition is promoted by this tendency of the oxide of manganese to pass into a state of higher oxidation. Oxalic acid, heated with strong nitric acid, is oxidized ; but when water is added, the oxidizing

action of the nitric acid ceases. If now a trace of manganous oxide in solution is added to the diluted mixture, oxidation recommences. Evidently there is some force residing in the oxalic acid tending to pull away the oxygen atoms from the nitric acid: with a certain dilution of the solutions an equilibrium is established, but this is at once upset by the introduction of the manganous oxide, which likewise tends to withdraw the atoms of oxygen. The higher oxide of manganese is, however, incapable of existing in an acid solution containing oxalic acid, which is thus enabled to take to itself the liberated oxygen, the manganous oxide remaining unchanged.

A very interesting instance of catalytic action, resulting in the liberation of oxygen, is seen in the action of heat upon solutions of the hypochlorites containing certain metallic oxides. If a strong and filtered solution of calcium hypochlorite, $\text{Ca}(\text{ClO})_2$ (from chloride of lime), is heated with a small quantity of precipitated cupric oxide to about 50° , oxygen to the extent of 30 times the volume of the solution is evolved, whilst the cupric oxide experiences no change. The oxides of cobalt, nickel, and iron will bring about the same decomposition. Many circumstances appear to show that the oxygen in calcium hypochlorite is very loosely held; if a solution of this body is exposed even to sunlight, oxygen is slowly evolved. But the manner in which the metallic oxide intensifies the force tending to withdraw the oxygen from the hypochlorite is not very apparent. Possibly the evolution of the oxygen may be due to *induced* action, as in the case of the manganese oxide, the oxides tending to pass into a higher but unstable state of oxidation; or possibly a metallic hypochlorite may be formed which is subsequently decomposed, the oxygen being liberated in the free state.

Various other methods of preparing oxygen will be described hereafter.

33. Properties of Oxygen.—By whatever method obtained, oxygen is a colourless, tasteless, inodorous gas, which has resisted every attempt to effect its liquefaction. It is 16 times heavier than hydrogen; therefore 1 litre at the standard temperature and pressure should weigh 16 criths or 16×0.0896 grams = 1.4336 grams. It is the least refractive of all

gases. Even at the ordinary temperature it manifests a marked chemical activity. If a piece of sodium or potassium be thrown into an atmosphere of the gas, combination occurs and an oxide of the metal is obtained. Phosphorus in bulk is slowly oxidized in contact with the gas; when finely divided, it bursts into flame, from the great heat developed in the rapid combination. Many other finely divided substances combine with oxygen, even when diluted with nitrogen; thus iron and lead, when obtained by chemical means in a state of minute subdivision, become oxidized, with the evolution of light and heat, if simply exposed to the air. The same effect is seen on massive iron in the formation of *rust*, which is simply ferric oxide (Fe_2O_3), produced by the action of oxygen in presence of atmospheric moisture and carbon dioxide; lead in mass, in like manner, is tarnished on exposure by the same action. A heap of rags or tow, saturated with oil and left exposed to the air, becomes heated from the oxidation of the oil, and not unfrequently inflames from the energy of the combination.

At increased temperatures the chemical activity of oxygen is greatly augmented. If the piece of phosphorus be gently heated, on plunging it into an atmosphere of oxygen, it bursts into flame and burns with dazzling brilliancy. If a jet of oxygen be allowed to play upon molten zinc, the metal burns with a very bright light. In like manner, a spiral of iron wire or a steel watch-spring, when heated sufficiently, may be made to burn brilliantly in oxygen. Indeed, all so-called combustible substances, when at a sufficiently high temperature, combine with oxygen with the evolution of more or less light and heat. A fragment of red hot charcoal or of feebly burning sulphur burn with greatly increased energy when introduced into a vessel filled with oxygen.

34. The Oxides.—The substances formed by the combination of the elements with oxygen are termed *oxides*; all the elements, with the exception of fluorine, are capable of combining with oxygen. If we pour a little lime water into the jar in which the charcoal was burned, we notice that it becomes turbid, owing to the presence of carbon dioxide, if we add a few drops of the tincture of litmus to the jars in which the phosphorus and sulphur were consumed, the

blue liquid is immediately reddened from the solution of the oxides of phosphorus and sulphur which are formed. A similar change of colour is brought about by the addition of any acid to litmus solution. Lavoisier first drew attention to the fact that the products obtained by the combination of Scheele's empyreal air with certain elements gave rise, on solution in water, to bodies which affected vegetable colouring matters in exactly the same manner as acids. Lavoisier concluded, therefore, that this air was the acidifying principle, and to denote this idea he proposed to change its name to "Oxygen," from *ὄξυς*, *acid*; and *γεννάω*, *I produce*. This view of the constitution of the acids—viz., that they necessarily contain oxygen—we now know to be erroneous, for many substances affecting vegetable colours in the manner described are without a particle of this element; other substances which do contain oxygen, such as the oxides of potassium and sodium, have an action totally different from that of the acids on the colouring matters; whilst a third class of oxides, for instance, those of iron and silver, are entirely without action.

The oxides are a very numerous and important class of substances; many of them, such as those of iron, manganese, tin, chromium, and copper, occur native, and constitute valuable ores. Some oxides, as we have seen, may be obtained by direct combination: others, as the oxides of silver, platinum, and gold, can only be obtained by circuitous methods. The majority of the oxides are solid at ordinary temperatures; they are usually opaque and earthy substances, destitute of lustre, and, with few exceptions, non-conductors of electricity. Some few are gaseous under ordinary circumstances, and a very few are liquid.

An element not unfrequently has the power of uniting with oxygen in several proportions. Thus, no fewer than five oxides of nitrogen are known, and even six oxides of manganese are supposed to exist. To designate the absolute position of the oxides in a series, we employ prefixes derived from the Greek numerals: thus, we have *monoxide*, *dioxide*, *trioxide*, *tetroxide*, *pentoxide*, &c. Occasionally the definition is not so precise, and the prefixes *proto* and *per* are employed merely to indicate the relative position of the oxides in the series.

35. Combustion.—All phenomena of burning are manifes-

tations of chemical action, accompanied by great heat and light, and resulting in the formation of chemical compounds. What we ordinarily term combustion is simply the act of chemical change rendered evident to us by the production of light and heat: viewed in this manner, the phenomenon is not restricted to the process of combination with oxygen; the copper burning in sulphur vapour, and the gun-cotton in the vacuum, are equally instances of combustion. Oxygen is said to be a *supporter of combustion*: combustible substances—bodies which take fire—burn in it, but the gas itself is not inflamed. Hydrogen is a combustible substance; when a lighted taper is brought to it, it takes fire at the mouth of the vessel in which it is contained, but the bulk of the gas does not momentarily inflame. We noticed that if the lighted taper is pushed up into the bulk of the gas, it is extinguished. As we express it, hydrogen is not a supporter of combustion. The air contains oxygen in the free state; it has been stated that every five volumes of air contain one volume of this gas. We have also seen that a candle in the act of burning combines with this oxygen: its combustion implies combination with oxygen. But, if the lighted candle be thrust into an atmosphere for which its constituents, even at the temperature of its flame, have no chemical affinity, the act of combination ends, and combustion ceases. The constituents of the candle have no tendency to combine with hydrogen; hence the candle is extinguished when plunged into that gas.

But the hydrogen burns at the mouth of the jar—it burns where it comes in contact with the oxygen of the air; for, as we have already stated, the act of hydrogen burning in the air means combination with oxygen to form water. We know that if we mix the air and hydrogen within the vessel, we shall have a very energetic combination on the approach of a light—an almost momentary combustion, attended with so much heat that an explosion results. Let us consider what would be the effect if hydrogen were substituted for oxygen in our own atmosphere. If, by some means, we brought a flame to a jar of oxygen situated in this atmosphere, *the oxygen would inflame* at the mouth of the jar—at the place where it meets with the hydrogen, *the oxygen would be the combustible* and *the hydrogen would support its combustion*. Obvi-

ously, therefore, the terms "supporter of combustion" and "combustible" are merely relative; they refer simply to the conditions under which we exist. It is very easy to show this

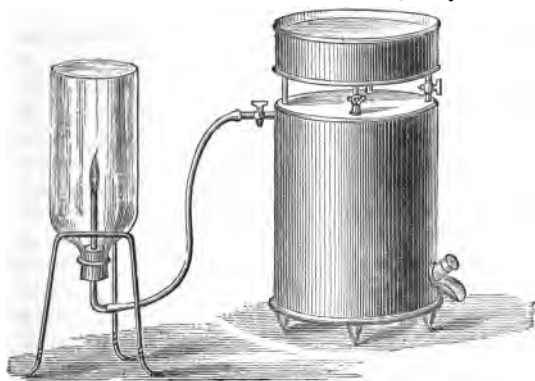


Fig. 31.

important fact, by actually causing oxygen to burn in an atmosphere of hydrogen. The large jar (fig. 31) contains hydrogen; if the gas be inflamed at the mouth, and a glass tube delivering oxygen from the gas-holder be pushed through the flame, the flame will follow the end of the tube in its upward progress into the jar, and by inserting the cork into the neck, the flame burning there will be extinguished (owing to the mixing of air and hydrogen being prevented); but the flame within the jar will continue to burn at the end of the tube where the oxygen first meets with the hydrogen.

By an experiment identical in principle, the air may be caused to appear as a combustible, and the common gas from coal, which we use to illuminate our houses, may be made to support its combustion. The flask in fig. 32 has two holes

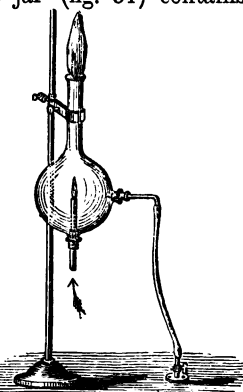


Fig. 32.

blown out before the glass-blower's lamp in its side; in one of the holes is fitted a cork carrying a short piece of glass tube, which is connected by means of caoutchouc tubing with the gas supply; through the other hole is pushed a short length of brass tubing, a cork-borer for example. The apparatus is filled with coal-gas, the excess of which may be kindled as it escapes from the upper mouth; if a lighted taper be quickly pushed up through the brass tube, the flame will appear at the end where the air first meets the coal-gas.

Energetic combustion is always attended with the evolution of great heat. This evolution of heat is the result of the chemical combination of the substances. It should be carefully borne in mind, however, that the aggregate amount of the heat produced is the same whether the combination takes years to accomplish, or is effected in a few minutes. Charcoal, for example, produces exactly the same combinations when burning in air as when burning in pure oxygen; and its union with oxygen, either pure or diluted, generates the same amount of heat in each case. The difference in temperature is due to the fact that air contains a large amount of nitrogen, a gas which acts as a diluent, and retards the contact of fresh portions of oxygen with the burning body. If, however, the motion of the air be increased, as by the action of the smith's bellows, a greater number of oxygen particles are brought into contact with the combustible in a given time, and therefore the rapidity of the combination and, accordingly, the temperature, are augmented. This principle regulates the action of all other contrivances, such as blowing-machines, dampers, &c., employed to modify the rapidity of combustion in air.

✓36. **Respiration.**—Oxygen is the life-supporting element in the air. The consumption of this body by the animal may be taken as the measure of its vitality. All animals require that this gas should be brought into close contact with the blood or internal juices of their bodies. The mechanism by which the oxygenation is principally effected varies in different animals. In man and in the higher air-breathing animals, air is drawn by the alternate expansion and contraction of the chest-walls into the lungs, and is thus brought into intimate contact with the blood contained in the ramification of

vessels situated over that organ. In some animals the air is carried through the system by means of minute tubes, and in many of the lower animals oxygenation is accomplished by a process of simple transpiration—that is, by the air making its way through the external surface of their bodies. Indeed, this process occurs also to a limited extent in the case of the higher animals, as in man. The earliest notions of men respecting the theory of respiration were exceedingly crude. The ancients generally considered that the object of the process was to moderate the animal heat. John Mayow, in 1674, first distinctly pointed out that respiration was attended with the absorption of a constituent of the air, and that this substance (which he also recognized as an ingredient of nitre) exerted a direct action upon the blood. Black, in 1757, showed that respiration resulted not only in the abstraction of something from the air during inspiration, but also in the returning of something to the air in expiration. But the true action of animals upon the air was first clearly established by Lavoisier, who, connecting together the results of his predecessors, showed that in the act of respiration animals inspire oxygen, and expire carbon dioxide; and he further pointed out that the high temperature which distinguishes animals from inanimate things could be accounted for on the supposition that it was due to the combustion of an amount of carbon in the blood, equal to that contained in the carbon dioxide expired. According to this idea, the lungs act as the furnace of the body. Animal heat is maintained by a process of chemical combination—of combustion in the lungs—identical in character with that manifested when charcoal burns in oxygen. As this combination takes place only in one spot of the body, whilst the temperature in all parts is nearly identical, Lavoisier further concluded that the rapidity of the circulation of the blood and the evaporation from the lungs were sufficient to maintain an equable temperature. It is very easy to show that carbon dioxide is a constituent of expired air: we need only to blow through a small quantity of lime water for a minute or so to obtain the turbidity characteristic of the combination of the lime and carbon dioxide. By means of the arrangement shown in fig. 33, the change effected in air on breathing may be

shown in a very conclusive manner. The apparatus consists of a couple of flasks connected together by a bent tube furnished with a side tube and mouthpiece;

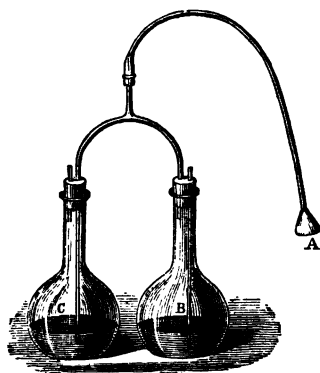


Fig. 33.

on inspiring air through this mouthpiece A, air is drawn in through the lime water contained in B, which remains unaffected; on blowing through the apparatus, the expired air is forced through the lime water in C, which rapidly becomes milky. The process of combustion, however, is not confined to the union of oxygen and carbon, for Lavoisier recognized that more oxygen disappeared than is returned to the air as carbon dioxide. This surplus amount, he supposed, might combine with the blood, or might—which he considered more probable—unite with its hydrogen to form water. But further experiment showed that this view of the action of oxygen could not be received in its entirety. It presupposed that the venous blood contained no dissolved gases, and that the carbon dioxide was only formed during the process of arterialization. It was observed that certain slow-breathing animals, placed in an atmosphere of hydrogen, continued to exhale carbon dioxide for a long time. This gas could not have arisen from the direct combustion of carbon: its quantity was far larger than corresponded to the amount of oxygen which could be supposed to be present in the lungs when the animals were removed from the air. By direct experiment it was shown that oxygen, nitrogen, and carbon dioxide were present in venous blood, as well as in that of the arteries: The following analyses will give an idea of the relative proportion of these gases in 100 volumes of the arterial and venous blood of a dog:—

	Oxygen.	Nitrogen.	Carbon Dioxide.		Total.
Artery,.....	16.29	0.93	28.39	=	45.61 c.c.
Vein.	8.22	0.95	34.26	=	43.43 c.c.

Hence it appears that, although both kinds of blood contain the same gases, venous blood contains more carbon dioxide and less oxygen than arterial blood. The views of physiologists were accordingly modified, and the combustion theory of Lavoisier was renounced: the action of oxygen was now considered to be purely physical. The venous blood charged with carbon dioxide in solution is brought, during its passage through the lungs, in contact with an atmosphere containing but little of that gas, and accordingly gives up a portion until an equilibrium is established between the amount contained in the lungs and that remaining in the blood: in like manner, being comparatively poor in oxygen, it takes up that gas until a similar equilibrium is established between the quantity in the blood and in the air of the lungs. Further experiments have shown that this diffusion theory must be again modified: it was pointed out that animals absorbed just as much oxygen when breathing an atmosphere of the pure gas as when breathing air, and also that the relations between the gas are in no-wise disturbed when the breathing occurs under diminished pressure, as at the top of a high mountain. It would appear from this that the absorption of oxygen is not purely physical; the gas must combine chemically with some constituent of the blood, but in so feeble a manner that very slight causes are sufficient to disturb the combination. Subsequent experiments have confirmed this conclusion, and have proved that the power of taking up the oxygen resides in the red corpuscles, and not in the serum in which they are suspended. The corpuscles of blood contain a crystalline substance called *hæmoglobin*, which has the power of taking up oxygen to form a body termed *oxyhæmoglobin*: this is red, and gives to arterial blood its characteristic colour. If the oxygen be removed, the substance is transformed into the original hæmoglobin, which is found to be purple. The absorption of oxygen is, therefore, supposed to take place through the agency of the hæmoglobin, which is transformed into oxyhæmoglobin, and changes in colour from purple to red in the course of its circulation; a portion of the oxyhæmoglobin again parts with its oxygen, and becomes once more reduced to purple hæmoglobin. But, as we have seen, venous or purple blood contains oxygen; it should therefore contain oxyhæmo-

globin to some extent, and such is found to be the case. Moreover, when an animal is asphyxiated, both the air in its lungs and in its blood is devoid of oxygen; the colour of the blood is turned to a full purple, and is observed to contain only hæmoglobin.

The elimination of oxygen from oxyhæmoglobin is only attended with change of colour from red to purple, when the body effecting the expulsion does not itself combine with the hæmoglobin. Many gases have the power of destroying the combination, and expelling the oxygen; and some of them, like carbon monoxide and nitric oxide, take the place of the oxygen expelled. The combination of carbon monoxide and hæmoglobin, termed *carboxyhæmoglobin*, is of a very bright red colour: blood containing this substance has lost the power of taking up oxygen, or of becoming arterialized. It is found that one gram of hæmoglobin absorbs equal volumes of oxygen, carbon monoxide, and nitric oxide, viz., 1.3 c.c. The amount of hæmoglobin in blood is not varied by going up to the top of a mountain, nor are the respirations in a given time greatly increased; provided there is enough oxygen for the purpose of combination, its increase or diminution exercise little or no influence on the economy.

The carbon dioxide in the blood is also held in a state of weak chemical combination with the inorganic salts which it contains. It has been shown that solutions of sodium phosphate and carbonate have the power of taking up notable quantities of carbon dioxide, and that they fail to part with this gas except under greatly diminished pressure, or by the action of heat. The blood contains these salts, and it is found that the same conditions are required artificially to break up the combination of the carbon dioxide in blood as in the saline solutions. It is not very clearly established what cause naturally effects the dissociation of the carbon dioxide: it has been supposed that the combination of the oxygen with the hæmoglobin is attended with the liberation of carbon dioxide in the blood, the tension of the liberated gas within the blood exceeds that contained in the lungs, and accordingly it escapes until equilibrium is established.

The volume of air expired is always less than that inspired when both are dried and measured at the same temperature. Since the nitrogen in the air is not sensibly absorbed by blood,

and oxygen gives its own volume of carbon dioxide, the decrease must be due to the retention of the gases within the system. The quantity named is not invariable, but on the average does not exceed 2 or 3 per cent. of the total volume inspired. The temperature of the expired air depends of course on the rate and mode of breathing, and on the difference in temperature between the air and blood, &c.: in general it is about 33° or 34°. It is usually almost saturated with aqueous vapour, but during fasting the amount of moisture decreases. It is calculated that on the average we expire about half a litre of water during 24 hours. During respiration, air loses from 4 to 5 per cent. of its oxygen, and gains from 3 to 4 per cent. of carbon dioxide.

It has already been stated that an interchange between the gases of the blood and of the atmosphere takes place in man by means of the skin; but the amount of the gases thus exchanged is comparatively small. It is found that the quantity of carbon dioxide so exhaled is about 4 grams in 24 hours. Fowls, rabbits, and dogs in like manner possess the power of cutaneous respiration. In the lower animals the skin plays a very important part in respiration. Frogs, which consumed .063 grams of oxygen per kilogram of weight per hour, consumed very nearly as much when their lungs were removed.

The quantity of carbon dioxide expired is greatest at the end of an expiration. During a given time, and for the same rate of breathing, the deeper the breath, the less is the percentage of carbon dioxide in the expired air, but the greater the total quantity exhaled. For a constant depth of breath, the quicker the rate of breathing the less is the percentage, but the greater the total quantity of carbon dioxide exhaled (M. Foster). No absolute relation has been traced between the temperature of the air and the carbon dioxide evolved. The increased amount in winter is mainly due to the increased quantity of oxygen taken into the lungs at each inspiration. Still it would appear that the seasons have an influence independently of change of temperature; the respiratory functions are most active in spring and least active in autumn. The amount of carbon dioxide expired decreases when the quantity contained in the gas inhaled is increased; if the tension of this gas, as in a confined atmosphere, exceeds, by continued

breathing, the tension of the gas in the blood, the carbon dioxide expired is re-absorbed. During starvation the amount of expired carbon dioxide decreases; it gradually increases during from one to two hours after a meal. During sleep the amount of carbon dioxide is diminished; this is very marked in the hibernation of animals. A hedgehog, which when awake exhaled 1.35 grams of carbon dioxide in an hour, produced when in a state of torpor only .006 gram per hour; similarly, a marmot produced 1.076 grams when awake, and only .1044 gram when torpid.

The following table gives the amount of oxygen consumed per hour per kilogram of body-weight by various animals:—

Sheep,.....	0.497 grams.	Fowls,	1.147 grams.
Calves,.....	0.480 „	Ducks,.....	1.850 „
Dogs,.....	1.183 „	Small birds,..	11.473 „
Rabbits,.....	1.714 „	Frogs,.....	0.084 „

37. Solubility of Oxygen.—Oxygen is slightly soluble in water; 100 volumes of the liquid dissolve about 3 volumes of the gas at ordinary temperature; the degree of solubility varies slightly with the temperature; 100 c.c. of water dissolve 4.1 c.c. of gas at 0°, and 2.8 c.c. at 20°. Small as these amounts may appear, the oxygen thus dissolved is the source of that required for the respiration of fishes. The breathing apparatus of fishes is peculiar to these animals. The water containing the dissolved oxygen is made to pass through the gills, and is thus brought in contact with a very thin membrane, round which the blood of the animal circulates, and through which the interchange of gases occurs. Some aquatic animals are furnished with a system of tubes or canals through which the water is carried to the various portions of the body.

CHAPTER IV.

THE ALLOTROPES OF HYDROGEN AND OXYGEN.

38. Allotropy—Isomerism.—In the foregoing pages we have had many examples of the modifying influence of

chemical action; but hitherto we have confined our attention to the action exerted between the atoms of dissimilar elements. The instances already adduced may be classed under the heads—(1.) Of chemical action exerted between two bodies to form a third substance totally differing from either of the colligating substances; (2.) Of chemical action exerted in the formation of two or more substances by the rearrangement of the atoms of a single substance; and (3.) Of chemical action exerted in the interchange of the atoms of two or more reacting compounds.

We have now to consider the effect of the rearrangement of the atoms in an elementary body.

It is an established fact that the same elementary substance may be possessed of widely different properties. By the action of various forces—heat, electricity, &c.—an element, such as hydrogen, oxygen, carbon, or phosphorus, may be changed completely in physical properties, as in colour, specific gravity, transparency, &c., and even in chemical activity. But the essential nature of the body is not altered; it is still elementary; that is, we are unable to get anything out of it differing from itself by any process of subtraction.

To indicate this fact—that the same substance can occur endowed with permanently different physical properties and chemical activities—the term *allotropy* (from *ἄλλος*, *other*; and *τροπος*, *mode*) has been proposed; the less frequent or latest discovered variety of a particular element is termed the *allotropic form or modification*, or the *allotrope*, of that element.

But this capacity for change in physical properties and chemical activity is not confined to the elementary bodies; it is possessed also by compound substances.

Instances are not wanting of bodies made up of the same elements united in the same proportion, and having identical molecular weights, yet differing very markedly in their chemical and physical relations. Such instances are less frequent in inorganic than in organic chemistry, where a very few elements are found to arrange themselves in many different ways. Thus we know of at least three distinctly different liquids possessing the formula $C_{10}H_{14}$, and having the same molecular weight, 134; these are, strictly speaking, allotropes

of one and the same body, *cymens*. It is usually preferred, however, to restrict the term *allotropy* to the elements, and to signify the same thing among compounds by the term *isomerism*. Thus, aldehyde, C_2H_4O , and butyric acid, $C_4H_8O_2$, are isomers. But, as instances multiplied, it became necessary to subdivide such bodies into two groups—(1.) Into isomers of identical, and (2.) into isomers of different, molecular weights. The former were termed *metamers*, and the latter *polymers*. Thus, di-ethyl-benzene, $C_6H_4 \cdot C_2H_5 \cdot C_2H_5 = C_{10}H_{14}$, and tetra-methyl-benzene, $C_6H_2(CH_3)_4 = C_{10}H_{14}$, are *metamers* of cymene or propyl-methyl-benzene, $C_6H_4 \cdot CH_3 \cdot C_3H_7 = C_{10}H_{14}$; whilst the numerous members of the C_nH_{2n} group (all having the percentage composition C 85.71, H 14.29) are *polymers* of ethene, C_2H_4 .

Numerous instances are known in inorganic chemistry of the same combination of elements crystallizing in essentially different forms, and possessing different specific gravities, colour, transparency, hardness, &c. Since these differences can only depend upon the rearrangement of the atoms in the molecule of the body, they may be said, strictly speaking, to be cases of isomerism. Thus, titanite oxide crystallizes in no less than three distinct forms—viz., as anatase (sp. gr. 3.826), rutile (sp. gr. 4.249), and brookite. Mercuric iodide separates from its solutions in the form of scarlet tables; but when sublimed these become rhombic, and their colour is changed to bright yellow. If these yellow crystals are allowed to cool slowly, they retain their colour; but if they are touched with a glass rod, they gradually become scarlet with a perceptible motion of their particles. Calcium carbonate crystallizes in one form as calcspar (sp. gr. 2.72), and in another as arragonite (sp. gr. 2.93.) A remarkable instance of isomerism is seen in the two pentoxides of antimony—the one modification is sparingly soluble in water, and is not dissolved by ammonia water; the other is dissolved by both of these liquids. The salts formed by the two acids are also perfectly distinct—the compounds of the more soluble variety are crystalline, those of the other are gelatinous and non-crystalline; the one class of salts gives precipitates with sodium compounds, the other forms no such precipitates.

There is a remarkable distinction between the isomers

of inorganic and organic chemistry, inasmuch as the former are mutually convertible, whereas the latter have a higher degree of permanence and stability. Thus, the modifications of the pentoxides of antimony, the calcium carbonates, and the mercuric iodides may be respectively transformed one into the other; whereas tetra-methyl-benzene and di-ethyl-benzene have not been found to be mutually convertible, or to become changed into propyl-methyl-benzene, although it is possible, indeed probable, that such changes may be effected.

39. Hydrogenium.—Many metals have the power of taking up hydrogen gas, and condensing or *occluding* it within their pores. Thus, if platinum, in the form of wire, be placed in a glazed porcelain tube, which, after being rendered vacuous, is heated to redness, and a rapid stream of hydrogen passed over it, the metal will absorb a certain amount of the gas. This may be recovered by again heating the metal in the exhausted tube, when, at the high temperature and diminished pressure, the gas will be liberated. The platinum thus treated absorbs about its own volume of hydrogen; in appearance it is not altered by the absorption, but after the expulsion of the gas it becomes white and blistered. Copper, gold, silver, and iron also take up hydrogen in amount dependent on their condition; when finely divided their capacity is increased. Iron takes up only about half its volume of hydrogen; but from certain extra-terrestrial specimens of the metal as much as three times their volume of the gas has been obtained; whence it is conjectured that these specimens have come from a stellar atmosphere of hydrogen denser than that of the earth.

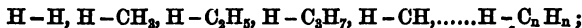
But of all the metals hitherto tried, palladium exhibits the highest power of absorption for hydrogen. Even at ordinary temperatures it takes up 376 times its volume of the gas; at 90° it occludes 643 volumes; at 245°, 526 volumes. When finely divided, it absorbs 686 volumes at 200°. The absorbed gas is slowly given off at ordinary temperatures, and rapidly at a red heat. In its condensed state this hydrogen appears to possess increased chemical activity. When the palladium holding it in occlusion is placed in solutions of iodine or chlorine, hydriodic or hydrochloric acids are rapidly formed;

if placed in solutions of ferric oxide, a portion of the combined oxygen is withdrawn, and ferrous oxide is produced. Vanadic acid dissolved in sulphuric acid is reduced to the state of vanadium dioxide.

If the palladium be presented to the hydrogen in the moment of its liberation in a chemical decomposition, the amount of the gas absorbed is largely increased. Zinc immersed in diluted sulphuric acid does not occlude hydrogen; but if palladium be placed in contact with the zinc, the former metal absorbs several hundred times its volume of gas. If the palladium be employed as the negative electrode of a battery of six elements of Bunsen's construction, more than twice the amount of hydrogen is absorbed than would be taken up by the same metal in an atmosphere of hydrogen. The hydrogen thus absorbed is not given off at ordinary temperatures even in a vacuum, but when heated to the temperature of boiling water it is readily expelled. Graham, by whom these phenomena were investigated, considered that the hydrogen was actually condensed, and that it alloyed itself with the palladium to form a combination having approximately the formula PdH_2 , analogous to the alloy we term brass, produced by the union of zinc and copper. Graham was led to believe that the hydrogen in this combination was condensed to the solid state and behaved like a metal, and to denote this modification of the element he proposed that it should be called *hydrogenium*. The alloy of hydrogenium and palladium has the same appearance as palladium. Assuming that it exists in combination, possessing the same density as in the free state and solid, Graham calculated, from the increase in volume observed to take place in the palladium after absorbing hydrogen, that hydrogenium had the specific gravity 0.733, water being 1. The tenacity of the alloy is slightly less than that of pure palladium; its power of conducting electricity is 5.99, whereas that of pure palladium is 8.10, when copper = 100. It is also more magnetic than palladium. Messrs. Wright and Roberts have, however, adduced important evidence on the constitution of the occluded hydrogen, which seems to throw doubt upon the chemical nature of the combination with the palladium.

In many of its chemical relations hydrogen exhibits very

marked analogies to the metals, and it has been often conjectured that when liquefied or solidified it would exhibit the physical characters of a metal. There is nothing extravagant in the supposition that a metal may be gaseous under ordinary conditions when in the free state: mercury itself is continually giving off vapour at all temperatures, and this gaseous mercury is affected by the circumstances of temperature and pressure exactly like a true gas. But hydrogen, as pointed out by Henry Watts, exhibits other analogies scarcely less marked than those of a metal. Thus, in the free state it may be assumed to be the starting point of a large and important class of organic compounds termed the *paraffins*; thus—



and from this relation we might with equal reason suppose that, if hydrogen were liquified or solidified, it would have the appearance of a transparent, colourless liquid, or of a solid, translucent, waxy-looking substance.

40. Ozone.—It has long been known that when an electrical machine is in full operation, a peculiar smell may be noticed in its immediate vicinity. This smell is due to the action of the silent electrical discharge upon the oxygen of the air, whereby it becomes transformed into an allotropic modification, to which, by reason of its peculiar odour, the name ozone (from *ὄζειν*, to *smell*) has been given. Von Marum first showed that it was the oxygen, and not any other principle in the air, which was acted upon by the silent discharge. By passing a series of discharges through pure oxygen he was able to give to that gas the peculiar odour noticed on working the electrical machine. The same body is produced during any manifestation of free electricity in the air. Its remarkable smell has frequently been observed after a succession of lightning flashes.

The first exact study of this body was made by Schönbein, in 1840; to him is due the name by which it is now known. He showed that it might be produced by a variety of methods, some of them purely chemical. Thus, if a piece of phosphorus be suspended in a jar of air containing a little water, so that it is partially immersed in the liquid, the air acquires the same odour as it obtains in the vicinity of the electrical

machine. The air is now found to possess increased chemical energy; it attacks mercury, and liberates iodine from potassium iodide. This last reaction may be employed as a convenient method of detecting the presence of ozone, particularly if the potassium iodide be mixed with starch, with which the liberated iodine has the power to form a combination of an intensely blue colour. The stick of phosphorus should be clean and freshly scraped, and the vessel should be rinsed out by a little *warm* water before its introduction. The phosphorus should not remain longer than an hour in the vessel, otherwise the amount of ozone will gradually diminish. On moistening a piece of paper with the mixed solutions of starch and potassium iodide and inserting it in the jar, the presence of ozone will be rendered manifest by the liberation of the iodine and the formation of the blue iodide of starch.

The oxygen evolved in the electrolytic decomposition of water (*vide infra*) contains ozone. Ozone may also be obtained by the action of strong sulphuric acid upon barium peroxide, and it is said to be produced in



Fig. 34.

the slow combustion of air and ether vapour. If a few drops of ether be poured into a large beaker, and strips of iodized starch paper and blue litmus paper be suspended within the vessel, on plunging a heated glass rod into the atmosphere of vapour and air, oxidation of the ether is set up, and an acid body and ozone will be formed, whereby the litmus paper will be reddened, and the iodized paper rendered blue. (Fig. 34.)

Ozone is produced in comparatively large quantity by the action of electrical discharges upon oxygen. The silent discharge is far more effective in bringing about the transformation than the spark discharge. The instrument represented in fig. 35 is well adapted to the production of ozone from oxygen. It consists of a glass tube, coated internally with tin foil, and placed in an outer tube, the outside of

which is also coated with tin foil. These coatings can be placed in connection with the wires from an induction coil; if the side-tube, *c*, be connected with a gasometer containing

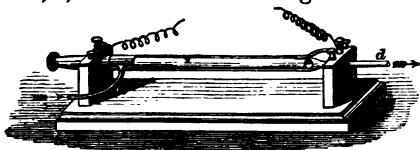


Fig. 35.

air or oxygen, and the gas be driven between the tubes, on passing the discharge, it will be found to be strongly ozonized as it leaves the exit tube, *d*. If a piece of glass tubing be pushed over *d*, and heated by a lamp, the issuing gas will no longer give the reactions of ozone, showing that at a high temperature this body is destroyed. The experiments of Andrews and Tait have shown that a temperature of 250° — 300° is sufficient to reconvert ozone into ordinary oxygen. This explains why the silent discharge is more efficacious in converting oxygen into ozone than the disruptive discharge; the high temperature of the spark tends to destroy the ozone as fast as it is produced.

Instead of the apparatus above described (known as *Siemen's induction tube*), the simple arrangement seen in fig. 36 may be employed. It consists of a piece of glass



Fig. 36.

tube, along the length of which is a platinum wire passing out through the caoutchouc tubing fixed to the end; on the outside of the tube is coiled a similar piece of platinum wire; when the two wires are placed in connection with a *Ruhmkorff's* coil, a slow stream of oxygen passed into the tube will become strongly charged with ozone. As much as from 60 to 120 milligrams of ozone per litre of oxygen may be obtained in this manner. Electrolytic oxygen contains only from 3 to 5 milligrams, and the gas from barium peroxide and sulphuric acid only about 10 milligrams per litre.

Ozone is oxygen in a condensed condition. If a quantity

of pure dry oxygen be submitted to the silent discharge, it is found to contract in volume; but, on being heated to 300° , it recovers its original bulk. This alternate contraction by the discharge and expansion on heating can be repeated indefinitely. If, after contraction, the gas be brought into contact with potassium iodide, the ozone is destroyed. The bulk of the gas, however, remains unaltered, but it no longer expands on being heated to its original volume—that is to say, the oxygen, absorbed by the reagent, occupies no bulk of the ozonized gas, as its removal does not diminish that bulk. On examining the solution of potassium iodide, it is found that the amount of the iodine liberated corresponds exactly to the oxygen which has suffered condensation. Mercury, on agitation with ozone, destroys that body; but the bulk of the ordinary oxygen formed is identical with that of the ozonized gas. These results may be explained on the supposition that, in contracting to ozone, 3 volumes of oxygen become 2 volumes, and that, on absorbing one-third of the combined oxygen by mercury or potassium iodide, the remaining two-thirds expand to their original bulk, or 2 volumes. Thus—

2 vols.

2 vols.



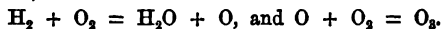
Ozone.

Oxygen.

Ozone, therefore, must have $1\frac{1}{2}$ times the density of oxygen; 1 litre, under the standard conditions of temperature and pressure, must weigh 24 criths or 2.15 grams. Observations on the diffusibility of ozone have established this conclusion.*

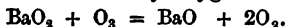
* We have seen that the rapidity with which a gas is translated varies in the inverse ratio of the square root of its density. Since $\sqrt{24} = 4.899$ and hydrogen moves with a mean velocity of 1,844 metres per second, it would follow that the ozone molecule should move with a mean velocity of 376 metres per second. Since the oxygen and nitrogen molecules move with a mean velocity of 461 and 492 metres per second, it might be possible to concentrate the ozone in an ozonized atmosphere by some process of atmolysis.

Ozone is produced in cases of rapid as well as of slow combustion. The combustion of all substances containing hydrogen in the air, or in oxygen, appears to generate ozone: thus, it is found surrounding the flames of hydrogen, alcohol, candles, coal-gas, &c. If a very narrow tube be presented to the lower edge of the flame of a Bunsen lamp, a *gentle* current of air aspirated through it will give all the reactions of ozone. Ozone is also formed when a strong current of air is blown through the upper portion of the flame. It is not formed during the combustion of carbon. The formation of ozone by the combustion of hydrogen in air may be accounted for on the supposition that the molecule of hydrogen separates the two atoms of the molecule of oxygen, one of which unites with the hydrogen to form water, whilst the other unites with another molecule of oxygen to form ozone (Than)—



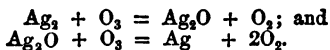
No ozone is formed in the combustion of carbon, for the reason that the combination of the combustible with the oxygen takes place by whole molecules of the gas.

Ozone displays a great tendency to throw off one of its atoms of oxygen, and to pass into the state of a molecule of the ordinary gas. By reason of the ease with which this is accomplished, it manifests very energetic oxidizing powers. It rapidly acts upon organic matter, corrodes caoutchouc, bleaches vegetable colours, and converts indigo into the colourless isatin. It oxidizes lead sulphide to lead sulphate, and converts the yellow potassium ferrocyanide into the red ferridcyanide. Many metals, whose oxides are only formed with difficulty, are readily oxidized by ozone. Thus, *moist* silver is converted into a peroxide. Many peroxides destroy ozone; in some cases these peroxides are partially *reduced* by the ozone: thus, barium peroxide, brought into an atmosphere containing ozone, is speedily reduced to the state of monoxide, whilst the ozone is converted into ordinary oxygen—



Ozone is rapidly destroyed by dry cupric oxide and manganese dioxide, but these substances experience no alteration. These catalytic actions are explained on the assumption that succes-

sive or simultaneous oxidations and reductions occur. Finely divided silver when dry also decomposes ozone in the same manner—



Ozone is very slightly soluble in water at low temperatures: 1,000 c.c absorb about 4.5 c.c of the gas (Carius).

CHAPTER V.

COMPOUNDS OF HYDROGEN AND OXYGEN.

HYDROGEN and oxygen combine together to form two compounds, viz :—

(1) HYDROGEN MONOXIDE, OR WATER, SYMBOL H_2O ; MOL. WEIGHT 18; DENSITY 9.

(2) HYDROGEN DIOXIDE, SYMBOL H_2O_2 ; MOL. WEIGHT 34.

41. Composition of Water.—We have already observed that hydrogen, or substances containing hydrogen, such as a paraffin candle, when burning in the air produce water; and we have also explained that the explosion caused by inflaming a mixture of oxygen and hydrogen is due to the rapidity and energy of the combination of these gases. When either of the gases is present in large excess, or when they are mixed with an inactive gas, such as nitrogen, the noise of the explosion is considerably diminished. Thus, the detonation produced by air and hydrogen is much less than that obtained from oxygen and hydrogen when mixed in certain proportions. In determining the exact proportions of the oxygen and hydrogen required to produce the greatest weight of water by explosion, Cavendish established, first, the compound nature of water; and, secondly, the relative proportions of its constituents. After innumerable trials, he found that the greatest weight of water from a given volume of the mixed gases, was produced when the oxygen and hydrogen were present in the proportion of one volume of the former to two volumes of the latter.

In order to determine the exact nature of the substance produced by the explosion, he made a mixture of the gases in the proportions of two volumes of hydrogen to one of oxygen in the graduated bell jar A, which was furnished with a stopcock, and stood in the pneumatic trough. (Fig. 37.) On to this stopcock he screwed a perfectly dry glass vessel, somewhat resembling that marked B in the figure; this also was furnished with a stopcock, and was evacuated by the air-pump. On opening the two stopcocks the mixed gases rushed into the empty vessel B, and, of course, the water rose proportionately in A. The stopcocks were again turned, and by means of two wires fastened into the top of B, an electric spark was passed into the midst of the gases, whereby they were instantly exploded. On again opening the stopcocks a further quantity of the mixed gases rushed into B, showing that the act of combination was attended with a great condensation in the bulk of the gases. After again shutting off the stopcocks the spark was again passed, whereby the gases were again combined. It had been previously noticed, and Cavendish confirmed the observation, that the sides of the vessel in which these explosions had occurred were bedewed with moisture, and that, as the explosions were repeated, the quantity of this moisture increased. This moisture he found to be pure water, and hence he deduced the conclusion that water is a compound substance.

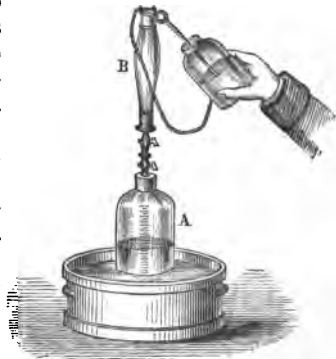


Fig. 37

By means of the arrangement seen in fig. 38, the fact that water is composed of oxygen and hydrogen, in the proportion of one volume of the former to two volumes of the latter, can be demonstrated in a more refined manner. The long and accurately divided tube *a*, called a *eudiometer*, is filled with mercury, and inverted in a cistern of the same metal. A quantity of pure hydrogen is then passed up into

the tube, and its volume is accurately determined. In order that the volumes of gases may be truly comparable, we require to know the temperature and pressure under which they exist. Accordingly, at the same time that we read off the

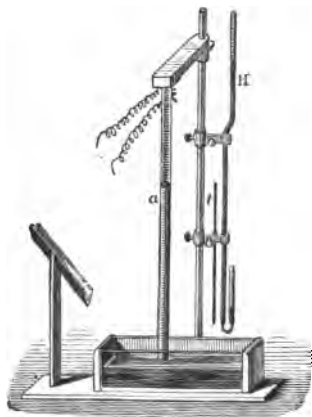


Fig. 38.

height of the mercury within the eudiometer, we also ascertain—(1) the temperature of the air, t , (and therefore of the gas within the eudiometer); and (2) the atmospheric pressure, H , from the barometer. The height of the barometer, however, does not directly give us the pressure to which the gas in the eudiometer is subject. If we were to sink the eudiometer in the mercury trough until the levels of the metal within and without the tube were coincident, we should notice that the volume of the gas would decrease. Under

these conditions only would the gas within the eudiometer be under the barometric pressure at the time of observation. When placed as in the figure, the confined gas is under diminished pressure, diminished by the height of the mercury column (h) above the level of the mercury in the trough, which tends to counterbalance the atmospheric pressure. The true pressure to which the gas is subject is therefore $P = H - h$. In order to facilitate the determination of h , the graduation on the tube is in millimetres. The temperature and volume of the confined gas are most accurately ascertained by the aid of a telescope placed at such a distance from the eudiometer that the heat of the body can exercise no disturbing influence. The confined volume of gas, V , must now be reduced to that which it would occupy under the standard conditions of temperature and pressure. The standard of temperature is 0° , that of pressure may be 1 metre of mercury.

$$V_1 = \frac{V(H-h)}{1 + 0.00366 \times t}$$

A quantity of pure oxygen is next passed up into the eudiometer, and the total volume of the mixed gases is again determined with all the above-mentioned precautions, and reduced to the standard conditions of temperature and pressure. The volume of the oxygen added is found by subtracting that of the hydrogen from the total volume of the mixed gases. The tube is now firmly fastened down against the bottom of the trough, and a spark from a Leyden jar or Ruhmkorff coil is passed into the midst of the gases by means of the platinum wires fused through the top of the eudiometer. A bright flash is seen to descend through the length of the tube, and, on releasing it from the bottom of the trough, the mercury rushes up to occupy the space of the combined gases. The volume of the condensed water is almost inappreciable—it occupies only about 1-2000th part of the mixed gases. The amount of the residual gas is again determined and reduced to 0° and 1 metre pressure, and its nature ascertained by inverting the tube and plunging a lighted taper into it. The volume of the residual gas, subtracted from the original amount of that gas, gives the quantity which has combined with the other gas to form water.

An example may render the process of calculation more clear.

1. Determination of volume of hydrogen—

Observed volume,	= 300 measures.
Temperature,	10° C.
Barometer,	0·765 m.
Height of mercury column in eudiometer,	0·400 m.

$$\text{Hence vol. of hydrogen } \left\{ \begin{array}{l} \text{at } 0^{\circ} \text{ C. and 1 m.} \end{array} \right\} = \frac{300 (0\cdot765 - 0\cdot400)}{1 + 0\cdot00366 \times 10} = 105\cdot6 \text{ measures.}$$

2. Determination of volume of hydrogen + oxygen—

Observed volume,	450 measures.
Temperature (t),	10·2° C.
Barometer (H),	0·760 m.
Height of mercury column (h),	0·20 m.

$$\text{Vol. of mixed gases at } 0^{\circ} \text{ C. and 1 m.} = \frac{450 (0\cdot76 - 0\cdot20)}{1 + 0\cdot00366 \times 10\cdot2} = 242\cdot7 \text{ vols.}$$

and $242\cdot7 - 105\cdot6 = 137\cdot1$ vols. of oxygen at 0° C. and 1 m.

3. Determination of volume of residual gas—

Observed volume,	281.9 measures.
Temperature (<i>t</i>),	10°
Barometer (<i>H</i>),	0.76 m.
Height of mercury column (<i>h</i>),	0.45 m.

$$\text{Volume at } 0^\circ \text{ C. and 1 m.} = \frac{281.9 (0.76 - 0.45)}{1 + 0.00366 \times 10^\circ} = 84.3 \text{ volumes.}$$

The residual gas was found to be oxygen. Accordingly, $137.1 - 84.3 = 52.8$ volumes of oxygen have combined with 105.6 volumes of hydrogen, or one volume of oxygen with two volumes of hydrogen, to form water.

It is important to ascertain the degree of condensation which the mixed gases experience in combining together to

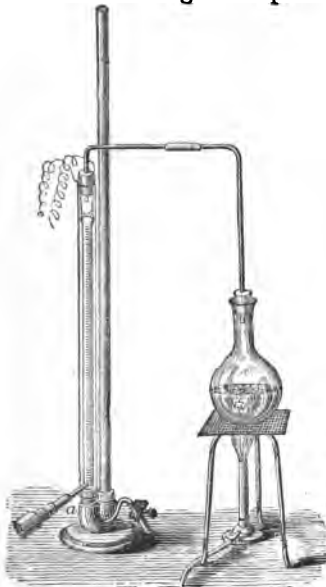


Fig. 33.

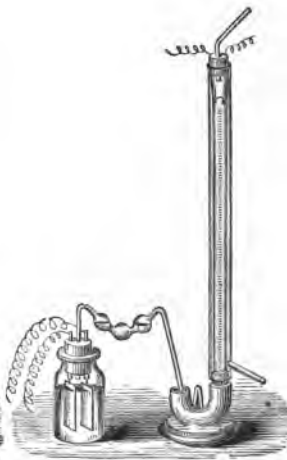


Fig. 40.

form the molecule of water. For this purpose it is necessary to compare the volume of the molecules before and after combination under identical conditions, and at a temperature

at which the water is in the state of a true gas. The arrangement represented in fig. 39 may be employed to determine this point.

Into the open ends of the iron U tube, *a* (such as is used to connect parallel steam-pipes), are fitted, by means of caoutchouc corks, two glass tubes, one of which is closed at the end, and furnished with two platinum wires melted into the glass. The iron U tube is attached to a heavy foot, and is provided with a side tube, which can be closed by a clamp compressing a short piece of attached caoutchouc tubing. The sealed tube is surrounded by a wider tube, open at the bottom and closed at the top with a caoutchouc cork; the bottom of the wide tube slips over the cork by which the sealed tube is fixed into the iron U tube. The upper cork is furnished with a tube leading to a flask containing amyl alcohol, which boils at 132°. A stream of the alcohol vapour is sent through the wide tube, and passes out through the side-tube at the bottom, into a condensing arrangement (not shown in full in the figure), in which it is again rendered liquid. The U tube and the sealed limb are completely filled with mercury, and a mixture of two volumes of hydrogen and one volume of oxygen (obtained by the electrolysis of water) is passed up into the sealed limb. Fig. 40 shows the method by which this is accomplished.* The open tube is again firmly fixed in its place, partially filled with mercury, and heated to 132° by passing the vapour of the boiling amyl alcohol through the wide tube; as soon as protracted boiling fails to increase the bulk of the gases, the levels of the mercury in the two limbs of the eudiometer are brought into coincidence by pouring more of the metal into the open limb, or by withdrawing some, if need be, by means of the side-tube and clamp. A thin caoutchouc band is then slipped over the outer tube to mark the volume of the heated gases, and a little more mercury is poured into the open limb, which is now securely closed by a caoutchouc cork. A spark from an induction coil is then caused to pass between the wires of the eudiometer, when the mixed gases combine with an explosion, the violence of which, however, is modified by

* This very convenient modification of the original apparatus of Hofmann is due to Professor J. P. Cooke.

the elasticity of the column of air confined between the cork and mercury. At the temperature of 132° , the water produced by the union of the gases retains the gaseous condition. On withdrawing the cork, and allowing the mercury

to flow out from the side tube until the levels of the metal in the limbs are again coincident, it is seen that the gases have contracted through one-third of their original bulk; in other words, three volumes of the mixed gases, made up of two volumes of hydrogen and one volume of oxygen, have combined together to form two volumes of steam. On removing the lamp from under the flask, the amyl alcohol ceases to boil, the steam cools down, and condenses to water.

We have thus effected the synthesis of water by volume: we now proceed to determine by analysis the volume-ratios of its constituents. This analysis is most conveniently effected by the electrolytic decomposition of the liquid. If water be acidified with a small quantity of sulphuric acid, so as to increase its conductivity, on immersing in it the electrodes of a sufficiently powerful battery-combination, gas bubbles will make their appearance on both plates.



Fig. 41.

The apparatus represented in fig. 41 may be conveniently employed to render this decomposition evident. The tubes A and B are furnished with stopcocks, and are connected together at the bottom. At their juncture is a side-tube, E, supporting a

long tube terminating in a large bulb, D. Through each of the tubes passes a platinum wire carrying a piece of platinum foil. Acidulated water is poured through D, and the cocks of A and B are opened until the tubes are completely filled. The stopcocks are then turned, and the electrodes connected with the wires of half a dozen cells of Grove's construction. The water is rapidly decomposed, and the evolved gas displaces the remainder of the liquid, driving it back into the tube D. In a very few minutes it is seen that a greater volume of gas is evolved from one pole than from the other, and on examination it is evident that the larger quantity comes from the negative or zinc pole. As soon as a sufficient quantity of gas has been evolved from both poles to admit of accurate measurement, it is seen that the gas from the negative pole occupies rather more than twice the bulk of that from the positive pole. On cautiously opening the cocks, the gases may be driven out through the jets, since they are under the pressure of the column of water in D; if a taper be brought to the mouth of the tube containing the gas from the negative pole, the gas will inflame: it is hydrogen. If the taper be brought to the mouth of the other tube containing the gas from the positive pole, the issuing gas will cause a more rapid combustion of the taper, showing that it is oxygen. It will be observed that the volume of the oxygen is *slightly* less than half that of the hydrogen. The difference is attributable to the greater solubility of oxygen, and to the fact that a portion of this gas is converted into ozone, whereby three volumes of oxygen become bound up in the space of two volumes. The presence of this ozone may be readily recognized by allowing the gas to impinge upon a moistened strip of iodized starch paper, which will be rendered blue. When due allowance is made for the cause of the slight divergence, it is evident that its electrolysis shows that water is made up of hydrogen and oxygen in the proportion of two volumes of the one to one volume of the other. The apparatus seen in fig. 42 serves

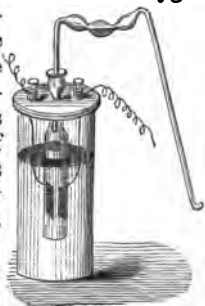
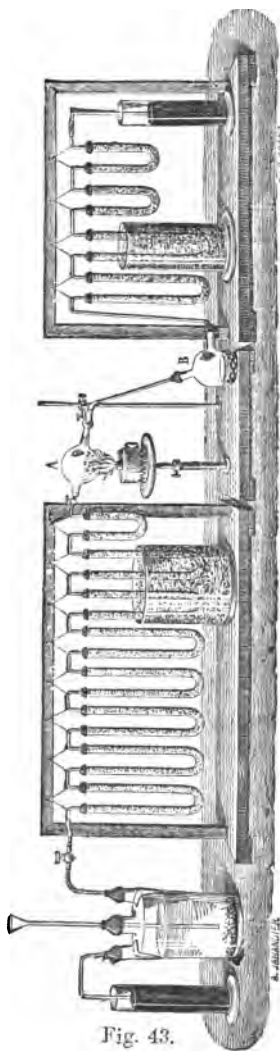


Fig. 42.



to collect the gases mixed in this proportion; the electrodes are placed together in the same vessel containing the acidulated water, and the electrolytic gas is evolved through the bent delivery tube.

Since oxygen has been found to be sixteen times heavier than hydrogen, it follows that these gases must be present in water in the proportion of sixteen parts by weight of oxygen to two parts by weight of hydrogen. It is desirable, however, that we should have the means of controlling this result, which, it will be remembered, has been deduced from our knowledge of the volume-weights of the two gases and the volume-ratios in which they combine. Many oxides—for example, copper oxide—when heated in hydrogen are reduced; their oxygen combines with the hydrogen to form water. If we determine the loss of weight experienced by the oxide, and weigh the water produced, we possess all the data required to determine the ratios by weight in which the two gases exist in water. The loss of weight suffered by the oxide gives the amount of oxygen; this weight subtracted from that of the water gives the amount of hydrogen. This synthetical method of determining the composition of water

by weight was originally proposed and carried out by Dulong and Berzelius, and was subsequently employed for the same purpose by Dumas and Boussingault. Fig. 43 represents the arrangement of the apparatus employed by these chemists. The hydrogen was generated from zinc and dilute sulphuric acid, and was purified by passing through a system of U tubes containing various absorbent materials; the last four tubes contained calcium chloride, to absorb any accompanying moisture; the terminal one was weighed before and after the experiment to demonstrate that the hydrogen was perfectly dry. Pure and dry hydrogen was thus driven into the bulb A, containing a weighed amount of cupric oxide in fine powder. On heating the oxide in the gas, water was formed, the greater portion of which was condensed in the vessel B, the last traces of moisture, carried away by the excess of hydrogen, being absorbed in the second series of U tubes containing calcium chloride; their increase in weight, determined by weighing them before and after the experiment, gave the amount of absorbed moisture. This weight, added to that of the bulb B, gave the total weight of water formed; the decrease of the weight of A, as determined by weighing it at the termination of the experiment, indicated the amount of oxygen in this water, the difference of course being the hydrogen. In an actual determination, Dumas and Boussingault found that a certain quantity of copper oxide heated in hydrogen lost 59.789 grams of oxygen, and yielded 67.282 grams of water. Hence $67.282 - 59.789 = 7.493$ grams. Accordingly the relation of the weight of the oxygen to that of the hydrogen is as 59.789 to 7.493, or expressed centesimally it is as 88.73 to 11.27. By taking the average of a great number of experiments, in which, as a rule, far larger quantities of water were obtained, it was found that the actual percentage composition by weight of water was—

Oxygen,	88.89 or 16.
Hydrogen,	11.11 or 2.

100.00

The difference between the numbers obtained from the result of the experiment quoted and those given as the average number of all the experiments, is due to unavoid-

able *errors of experiment*; provided that the experiments are done with due care, these errors may be eliminated by taking the mean result of a large number of observations.

42. The Oxyhydrogen Flame.—It has already been stated that the combination of oxygen and hydrogen is attended with the production of much heat. By bringing a jet of oxygen within a flame of hydrogen a very intense heat (calculated to be about $2,800^{\circ}$) may be produced. The flame of the mixed gas is very slightly luminous; but, if projected on a piece of lime, it raises the temperature of that earth to

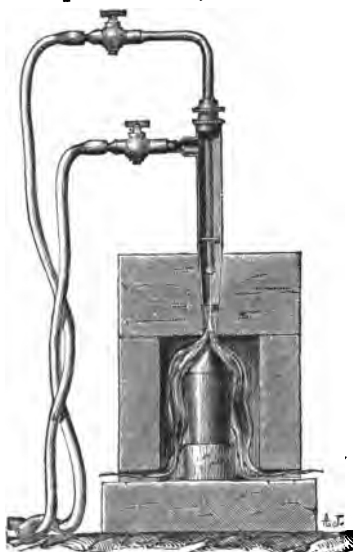


Fig. 44.

whiteness; iron wire or a watch spring burn with brilliant scintillations; a piece of platinum, which is one of the most infusible metals, may be readily liquefied; and silver may even be made to boil and to distil by the heat of the flame. The intense heat of the combination is turned to useful account in smelting refractory substances, or in fusing metals like platinum, which require a very high temperature to bring about their liquefaction. Fig. 44 represents a variety of furnace employed for such purposes, made of blocks of well-burnt lime; the metal to be fused is placed in a crucible of gas carbon, which is placed in another crucible made of lime; the gases are forced from separate gasometers into two concentric copper tubes, the hydrogen being delivered into the outer, the oxygen into the inner one.

43. Properties of Water.—Pure water is a tasteless, odourless liquid, possessing, when viewed in bulk, a slight bluish-green colour. This colour is well seen in many deep

lakes, and may readily be observed by looking at a shining white object through a column of distilled water about 2 metres in length, contained in a tube with blackened sides. Water is about 770 times denser than air. It is almost incompressible; under an additional atmosphere 1,000,000 volumes of water become lessened by about 50 volumes. Water is a very bad conductor of heat. If a piece of ice, wrapped in wire gauze, is dropped into a test-tube containing a quantity of ice-cold water, the liquid may be heated to the boiling point at the surface before the ice at the bottom is appreciably melted.

44. Purification of Water by Distillation.—Absolutely pure water is seldom, if ever, found in nature. The water required for chemical purposes in general requires to be purified by *distillation*. This operation consists in vaporiz-

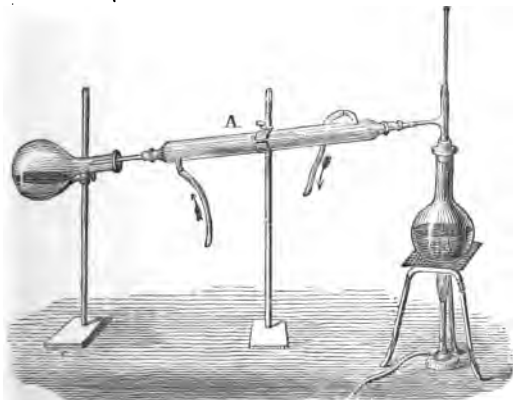


Fig. 45.

ing the water, and condensing the steam; the solid impurities are left behind in the evaporating vessel. (Fig. 45.)

45. Purification of Water by Filtration.—Water may be freed from suspended matter by *filtration*—that is, by allowing it to percolate through some medium, of which the pores are sufficiently fine to arrest the solid matter without interfering with the movement of the liquid. In the laboratory, filtration is usually effected through calico or

unsized paper. The paper is folded and placed in a glass or porcelain funnel, into which the turbid liquid is poured. The rapidity with which the liquid filters is dependent on the difference between the pressure exerted on its upper and lower surfaces. By increasing the pressure on the upper

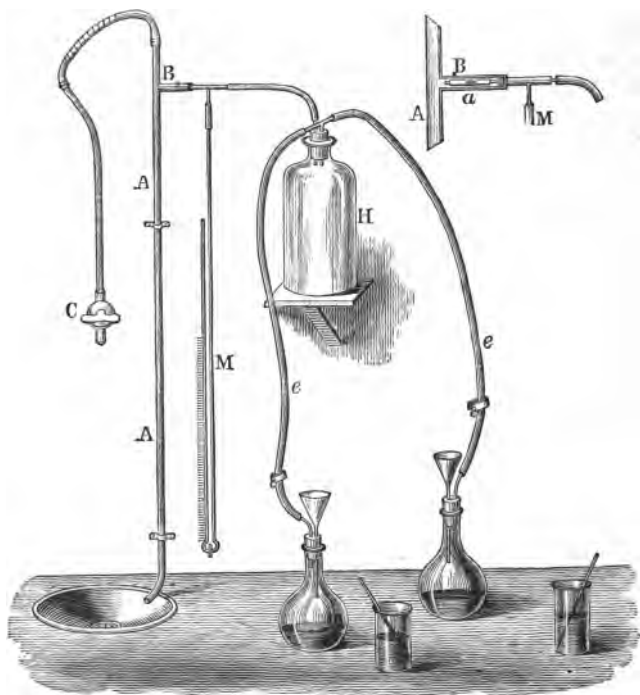


Fig. 46.

surface, or diminishing that on the lower, we proportionately increase the rapidity with which the liquid passes through the filter. Fig 46 represents a simple apparatus by which this difference in pressure may readily be brought about. A A is a brass tube about 1 metre in length, and from 8 to 10 millimetres in diameter, to the side of which is affixed

a side-tube, B, about 1 centimetre in length. The upper end of the vertical tube A is cut obliquely, and is connected by means of a strong but sufficiently elastic caoutchouc tube, with the stopcock C, in connection with the water supply. A Bunsen valve is fitted into the side-tube—that is, the caoutchouc tube *a* is stopped at the upper end with a short piece of glass rod, and cut along its length near the end by a smart blow from a chisel. The edges of the slit are thus left sharp, and on applying any outward pressure to the tube they readily adhere, making a perfectly air-tight conjunction. This valve is within the tube B, into which the caoutchouc tube fits perfectly air-tight. The other end of the tube is connected with a flask to receive the filtered liquid. A caoutchouc cork, pierced with two holes, fits into the neck of the flask; through one of the holes the stem of the funnel containing the filter paper is inserted, through the other is a glass tube bent at right angles, to which the tube *e*, leading to the intermediate vessel, is attached. On allowing the water from the main to flow through the vertical tube, the caoutchouc tube commences to pulsate rapidly as it falls over the upper edge of the tube A, and periodically closes the opening. The Bunsen valve intermittently opens and shuts, and rapid suction is set up, and it is easy to diminish the pressure within the flask to within one-twentieth of its original amount. A manometer, M, is fixed to B: this allows the degree of exhaustion to be immediately ascertained from the position of the mercury along the graduated scale. The intermediate vessel, H, allows of the simultaneous exhaustion of a number of filter flasks. The rapidity of the filtration may be regulated by the screw clamps on the tubes *e e*.

On the large scale, as in the purification of water for the supply of a town, it is filtered through beds of sand and gravel, arranged in the following order of descent:—fine sand; coarser sand; shells; fine gravel; coarse gravel. In some works the layers of the filtering substances are placed not uniformly flat, but are disposed in waves, and at the lowest point of each wave is placed an earthenware pipe which conducts away the water to the mains for distribution. The upper layer of sand requires frequent renewal, but the main portion of the filter may be used for many years.

46. Solution.—No neutral liquid surpasses water in its solvent action, that is, in its power of liquefying solid or gaseous bodies brought into contact with it, so that their particles become uniformly diffused through it, without tendency to separate out again on standing.

In chemical terminology, the liquid absorbing or liquefying the gas or solid is called the *solvent*, or, occasionally, the *menstruum*. The process of absorption or liquefaction, and also the product of the process, is termed a *solution*.

In speaking of the mutual action of liquids, it is usual to restrict the term *solution* to cases of partial miscibility; thus, if we agitate ether and water together, the two liquids do not, so to say, become intimately blended and lose themselves in each other: on allowing the agitated liquid to stand at rest, the greater number of the ether globules run together and rise to the surface of the water.

On examining the supernatant ether, however, it will be found to contain a notable amount of invisible or dissolved water; whilst the water on which it swims has taken up a considerable quantity of ether. The lower liquid would be termed an aqueous solution of ether; the upper one an ethereal solution of water.

Taking water as the typical liquid, we will now proceed to the consideration of the laws regulating the solution of gases and solids.

47. Absorption of Gases.—The various gases are all more or less soluble in water. The amount of any gas taken up by water (or by any other liquid on which that gas exerts no chemical action) is dependent—(1.) On the specific nature of the gas; (2.) On the temperature of the liquid; and, (3.) On the pressure under which the absorption is effected.

(1.) Water, as we have already seen, dissolves at 0°C . 1.9 volumes of hydrogen and 4.1 volumes of oxygen per cent. This proves that the amount of gas absorbed by the liquid varies with the nature of the gas. These gases are among the most insoluble in water: 100 volumes of water at 0° absorb 179.7 volumes of carbon dioxide, and upwards of 114,900 volumes of ammonia gas.

(2.) As a rule, we find that the volume of the gas absorbed by water decreases with its increase of temperature. Thus, it

was stated that, whereas 100 volumes of water at 0° dissolved 4.1 volumes of oxygen, the same volume of water at 20° absorbs only 2.8 volumes. Thus, too, whilst 100 volumes of water at 0° absorb about 114,900 volumes of ammonia gas, they only absorb 69,060 volumes at 20° . We have an exception to this law in the case of hydrogen, which is dissolved to the extent of 1.93 volumes per cent. of water at all temperatures between 0° and 25° .

(3.) The relation between the volume of a gas absorbed by water and the pressure under which the absorption occurs admits of a very simple expression. *The volume of the gas absorbed varies directly with the pressure.* This law was enunciated by its discover, William Henry, in these words: "Under equal circumstances of temperature, water takes up in all cases the same *volume* of condensed gas as of gas under ordinary pressure. But as the spaces occupied by every gas are inversely as the compressing force, it follows that water takes up of gas condensed by one, two, or more additional atmospheres, a quantity which, ordinarily compressed, would be equal to twice, thrice, and so on, the volume absorbed under the common pressure of the atmosphere."

The pressure exerted by a mixture of gases is equal to the aggregate effect of the impacts of its constituent molecules. If the mixture contains equal volumes of two gases, A and B, the effect of A's molecules will be half of that of A+B. But since the amount of gas absorbed varies with the effect exerted by the molecules, or, in other words, varies with the pressure under which the absorption is effected, it follows that the amount of A actually absorbed from the mixture can only be half of that which would have been absorbed if the entire pressure had been exerted by A. And what is true of A is equally true of B: by parity of reasoning it can be shown that it must be true of a mixture containing any number of gases.

The amount of each gas absorbed by water from a mixture is solely dependent upon the individual pressure exerted by that gas. This law, regulating the absorption of mixed gases by water, was first stated by Dalton; it is known as the law of "partial pressures." Dalton further showed that the limit to the absorptive action of water on a gas is gained

when the tensions of the gas within and without the liquid are in equilibrium. This means that the *amount* of gas in the liquid at any two given moments, under these conditions, is the same, for the molecules within the liquid are not quiescent, a constant interchange is going on from gas to liquid, and from liquid to gas. That this is the case may be

proved by placing the liquid in a gaseous atmosphere of another kind, when it will be found that the latter gas rapidly finds its way into the water, whilst the one previously absorbed may be detected in the atmosphere above.

Dalton's explanation of the process of solution failed, however, to account for the fact that the various gases, whose molecules we are to suppose are of equal size, are absorbed by water in different volumes. We are driven to the conclusion that the molecules of the gases within the water must be in some way altered in their relation to each other; probably they are brought so near to one another that the force of cohesion is brought into play, and they tend to pass from the truly gaseous condition.

The laws regulating the absorption of gases by liquids were

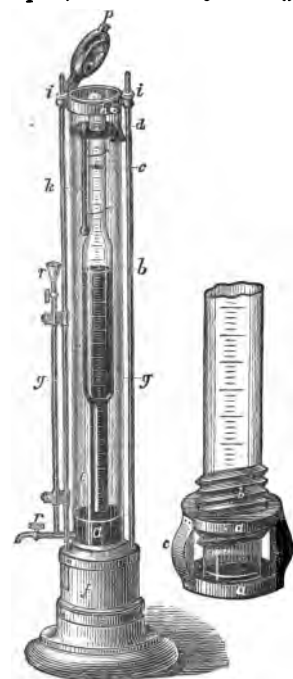


Fig. 47.

first experimentally studied with accuracy by Bunsen. The methods adopted by this chemist depended on the degree of solubility of the various gases. In the cases of the more soluble gases, such as ammonia and sulphuretted hydrogen, the amount absorbed was determined by estimating the gas existent in the liquid by means of chemical analysis; for

example, the sulphuretted hydrogen was converted into barium sulphate, which was weighed, and from its weight the quantity of the gas was calculated from the knowledge that $\text{BaSO}_4 = \text{H}_2\text{S}$. The experiments were repeated at various temperatures, and were properly corrected for the fact that the volume of the liquid is increased by the absorption of the gases.

The absorption of the more insoluble gases was determined by means of the *absorptiometer*, which is represented in fig. 47. It is thus described by Bunsen:—The absorption tube, *e*, divided into millimetres and calibrated (*i. e.*, the relative values of the several divisions, accurately determined) has a small iron band, *b*, fig. 47, furnished with a screw luted on its lower and open end; this fits into another screw attached to the small iron stand, *a a*. By means of this arrangement the open end of the tube can be screwed down against a plate of caoutchouc covering the bottom of the stand, and the tube thus completely closed. On each side of the stand are fixed two steel springs, *c c*, which fit into two vertical grooves inside the wooden foot of the apparatus, *f*, fig. 47, so that the little iron stand, *a a*, fig. 47, can be raised or depressed, but not turned on its axis, horizontally. The outer cylinder, *g g*, fig. 47, is not cemented into the wooden foot, *f*, nor into the iron rim, *h*, but the ground glass edges of the cylinder are pressed against caoutchouc rings inserted in the foot and in the rim by means of the screws, *i i*. The tubes, *r r*, serve to pour in mercury, so that any desired pressure is obtained in the absorption tube by raising or depressing the level of the mercury in the inner glass cylinder. The temperature of the surrounding water is determined by the small thermometer, *k*. The upper end of the glass cylinder is closed by an iron lid having a hinge at one side, and fastened down by means of a nut and screw attached to the iron rim, *h*, fitting into a groove, *p*, in the side of the lid. In the inside of the lid there is raised a rim of iron, over which a thick sheet of caoutchouc is extended and fastened by a screwed ring, *s*. This distended caoutchouc serves as a spring, against which the top of the tube can be pressed, keeping it in a fixed position during the violent agitation necessary for the process of absorption.

The tube, *e*, was filled with mercury at the trough, and a

quantity of nitrogen, for example, was passed up into it. The volume of the gas employed was determined with all the precautions already described. A quantity of water, perfectly free from air, was passed up into the tube, which was then tightly screwed against the caoutchouc plate *a*, and the whole was placed in the cylinder, *g g*, containing some mercury, and filled up with water. The pressures within and without the tube were equalized by releasing it slightly from the caoutchouc plate, when it was again closed. The iron lid was fastened down, and the apparatus vigorously agitated. The tube was again released to equalize the pressure, again screwed down, the lid was again closed, and the apparatus again agitated; this operation being repeated until no further diminution of the volume of the gas was perceptible. The volume of the water was determined by reading off its upper and lower level in the tube, *e*. The diminution of the original volume of the gas corrected for the pressure which it is under in the absorptiometer, gave the amount absorbed by the water at the temperature indicated by *k*.

Since, as we have seen, the solubility of a gas in a given liquid varies with its temperature and the pressure under which the absorption occurs, it is necessary, before we can compare the solubilities of gases, to fix upon—(1.) a definite volume of liquid, and (2.) upon its temperature, and (3.) upon the pressure of the absorption. It is usual, therefore, in stating the solubility of a gas, to express the volume of that gas at 0° C. and under a pressure of 0.76 m., absorbed by 1 c.c. of liquid at the temperature of observation, and under a pressure of 0.76 m.; the number expressing the volume of the gas is termed the *absorption-coefficient* of that gas for that liquid at the given temperature. Thus, the coefficient of absorption for nitrogen in water is 0.02035 at 0° C. and 0.01403 at 20°; that is, 1 c.c. of water at 0° C. absorbs 0.02035 c.c. of nitrogen (measured at 0° and 0.76 m.) under a pressure of 0.76 m.; and 1 c.c. of water at 20° absorbs 0.01403 c.c. of nitrogen (measured at 0° and 0.76 m.), under a pressure of 0.76 m.*

* Compare Bunsen's *Gasometry*, translated by Roscoe; also the article "Absorption of Gases," by Roscoe, in Watt's *Dictionary of Chemistry*.

The amount of gas absorbed by water increases, as we have seen, with its decrement of temperature, but this is true only so long as the water remains liquid. When it becomes ice, the dissolved gas escapes. But it is important to know that carbon dioxide, ammonia, and indeed all the gases which have been liquefied, are not expelled in the formation of ice. A very interesting instance of this fact is seen in the phenomenon termed the "spitting" of silver; when the metal is melted, it absorbs about twenty-two times its volume of oxygen from the air; as it solidifies, the gas is expelled with the appearance of ebullition, and portions of the metal are often forcibly projected from the crucible.

48. Solubility of Solid Substances.—We notice the same wide difference in the solubility of solid substances in water as of gases. Thus, whilst a litre of water at the ordinary temperature dissolves only 0.14 grams of strontium sulphate, the same quantity of water can take up nearly its own weight of crystallized magnesium sulphate; and whilst this quantity of water dissolves only 0.1 gram of calcium carbonate, it can dissolve nearly one-fourth of its weight of anhydrous sodium carbonate.

The rapidity with which a soluble substance dissolves is dependent to a great extent on the state of division of the solid. The more finely divided it is, the more rapidly it is dissolved. The rapidity with which fresh portions of the liquid are brought into contact with the solid also materially affects the rate of solution. If the soluble body in large pieces is placed at the bottom of the vessel containing the solvent, and the whole is maintained perfectly quiet, the rate of solution will be very slow. It is retarded by the layer of liquid contiguous to the substance becoming saturated, and this, by reason of its superior density, protects the undissolved portion from the further action of the solvent. Under these circumstances, solution proceeds by *liquid diffusion*—a process analagous to that of gaseous diffusion, but of infinitely less rapidity.

Graham, by whom the phenomena of liquid diffusion were minutely investigated, has established—(1.) That different salts, in solutions of equal strength, diffuse unequally in equal times. (2.) That with each salt the rate of diffusion increases

with the temperature, and at any given temperature is proportionate to the strength of the solution, at least when the quantity of salt dissolved does not exceed 4 or 5 per cent. (3.) Classes of equi-diffusive substances exist, which coincide in many cases with the isomorphous groups. Thus, the same rate of diffusion is exhibited by hydrochloric, hydrobromic, and hydriodic acids; by the chlorides, iodides, and bromides of the alkaline metals; by the nitrates of barium, strontium, and calcium; the sulphates of magnesium and zinc, &c., &c. (4.) For several groups of salts, it is found that the squares of the times of equal diffusion, from solutions of the same strength, stand to one another in a simple numerical relation. Thus, the *diffusate* from a solution of potassium nitrate in seven days was equal to that obtained from an equally strong solution of potassium carbonate in 9.9 days, numbers which are to one another as $1 \cdot \sqrt{2} = 1.414$. Similar results were obtained with 2 per cent. solutions of nitrate and sulphate of potassium, equal diffusates of the two being obtained in 2.5 and 4.95 days, in 7 and 9.9 days, and in 10.5 and 14.85 days; also with hydrate and nitrate of potassium, and with nitrate and carbonate of sodium. The times of equal diffusion of 1 per cent. solution of ammonium chloride and sodium chloride were to one another as $\sqrt{2} : \sqrt{3}$. Now, according to Graham's experiments, the squares of the times of equal diffusion of gases are to one another in the ratio of their densities. Hence, by analogy, it may be inferred that the molecules of these several salts, as they exist in solution, possess densities which are to one another as the squares of the times of equal diffusion. Thus, the solution-densities of sulphate, nitrate, and hydrate of potassium, are to one another as the squares of the numbers 4, 2, and 1—that is, as 16, 4, and 1. These solution densities appear to relate to a kind of molecules different from the chemical atoms, and the weights of which are either equal, or bear to one another a simple numerical relation.

The diffusion of a salt into the solution of another salt takes place with nearly the same velocity as into pure water—at least when the solutions are dilute. Graham has shown that the diffusion of a 4 per cent. solution of sodium carbonate is not sensibly affected by the presence of 4 per cent.

of sodium sulphate in the liquid atmosphere; nor that of a 4 per cent. solution of potassium nitrate by the same proportion of ammonium nitrate. The presence of 4 per cent. of sodium sulphate reduced the diffusion of sodium carbonate by only one-eighth of the whole. In stronger solutions the retardation would probably be greater. There is, indeed, reason to believe that the phenomena of liquid diffusion are exhibited in their simplest forms only by weak solutions—the effect of concentration, like that of compression in gases, being to produce a departure from the normal character. The rate of diffusion is, however, materially affected when the liquid atmosphere already contains a portion of the diffusing salt. The consideration of this case leads to the general question of the motion of particles of a dissolved substance in a solution of unequal concentration. The general law which regulates such movements appears to be this:—The velocity with which a soluble salt diffuses from a stronger into a weaker solution, is proportional to the difference of concentration between two contiguous strata. (*Watt's Dict.*, vol. iii., p. 708.)

As a general rule, the solubility of a solid in a liquid increases with the rise of temperature. A point is at length reached, when no more of the solid is dissolved in the liquid, which is then said to be *saturated*. Among the exceptions to the law may be mentioned lime, which is twice as soluble in water at 0° as in water at 100°; strontium sulphate, which requires 7,000 parts of water at 14°, and 9,600 parts at 100° for solution. Certain hydrated salts exhibit a maximum degree of solubility at temperatures but slightly above the ordinary temperature, a further increment of heat causing a precipitation of the dissolved salt. Thus, calcium sulphate is most soluble in water at 35°, 1 part of the salt dissolving at that temperature in 393 parts of water, at 0° in 488 parts, and at 100° in 460 parts (Poggiale).

It very frequently happens that a saturated solution of one substance can dissolve a certain amount of another body without any precipitation occurring. This fact is occasionally taken advantage of in analytical chemistry. Saturated solutions at any particular temperature may be prepared either by heating the liquid in contact with an excess of the solid

to the required temperature, or by heating it more strongly, and allowing the solution to cool down to the same point. In the generality of cases the saturated solution contains the same amount of the substance, by whichever way it is prepared. But when certain salts rich in water of crystallization, and especially those which have the power of crystallizing with water in different proportions, are dissolved to saturation in hot water, and the solutions allowed to cool out of direct contact with air, they frequently retain in solution at the lower temperature a far larger quantity of the salt than would be dissolved if the water and salt had remained in contact at that temperature. These solutions are said to be *super-saturated*. Very slight causes are sufficient to cause the precipitation of the excess of dissolved salt: if the solution be agitated, if dust or a particle of the solid salt be allowed to fall into the liquid, the salt suddenly separates out to such an extent that the whole appears to solidify, and a considerable rise of temperature is observed.

These phenomena are seen to perfection in the cases of sodium sulphate, acetate, and thiosulphate. A wide-mouthed flask of about 200 c.c. capacity is nearly half-filled with roughly powdered crystallized sodium thiosulphate $\text{Na}_2\text{S}_2\text{H}_2\text{O}_4 + 4 \text{H}_2\text{O}$, and placed in a large beaker of water, maintained at a temperature of 60° , until the salt is completely melted in its water of crystallization. The flask is then removed and placed upon some badly conducting surface, as a piece of flannel; in about three hours the liquid will have cooled down to the temperature of the air, when, on dropping a piece of the salt into the solution, the liquid will appear to solidify, and the temperature of the mass will be increased by 18° or 20° . Sodium acetate $\text{C}_2\text{H}_3\text{O}_2\text{Na} + 3 \text{H}_2\text{O}$ melts at 75° in its water of crystallization, and the liquid may be even cooled down to 0° without solidifying; on agitation, or in contact with a piece of the salt, the whole becomes solid, and the temperature, by the use of 200 grams of salt, rises through about 40° (from 11° to 54°). Many other salts, such as the alums, sodium phosphate, &c., exhibit similar phenomena, but with the difference that their supersaturated solutions cannot be cooled down to the ordinary temperature of the air without solidifying; in all cases, however, a rise of temperature

similar to that exhibited by the sodium salts above mentioned is exhibited when they solidify. We shall have occasion to return to the consideration of these phenomena in speaking of the elevation of temperature exhibited by water in the act of solidification, when previously cooled down below its freezing point.

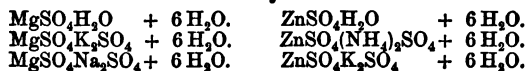
49. Water of Crystallization.—Many substances owe their crystalline character to the water which they hold in a state of chemical combination. Thus, sodium carbonate, $\text{Na}_2\text{CO}_3 + 10 \text{H}_2\text{O}$, crystallizes in large transparent crystals, belonging to the monoclinic system (see *Crystallography*); on allowing the crystals to remain exposed to the air, they gradually lose their transparency and *effloresce*—i. e., crumble to powder by giving up their *water of crystallization*. The peculiar form of this hydrate is due essentially to the water of crystallization with which it is combined. Various hydrates of sodium carbonate are known crystallizing in different systems; thus, the salt, $\text{Na}_2\text{CO}_3 + 7 \text{H}_2\text{O}$, crystallizes in forms belonging to the rhombic system; its appearance is totally different from that of the deca-hydrate, showing that the crystalline form of the salt is determined not only by the presence, but also by the relative amount of the water. Many salts, however, crystallize without water of combination; thus, common salt (NaCl) usually crystallizes in cubes—i. e., in the simplest crystallographic form; but it is possible to obtain this body in combination with two molecules of water, $\text{NaCl} + 2 \text{H}_2\text{O}$, when it crystallizes in forms derived from the triclinic—i. e., the most complicated crystallographic system.

The presence of water in a salt not only determines its crystallographic form, but also frequently modifies its colour to a remarkable extent. Thus, copper-sulphate, $\text{CuSO}_4 + 5 \text{H}_2\text{O}$, crystallizes in large azure-blue transparent triclinic prisms, which on heating to 200° become anhydrous and white. The same effect can be brought about by immersing the crystals in strong sulphuric acid, which has so great an affinity for water that it is able to abstract it from the salt. Cobalt chloride when anhydrous is blue, but when dissolved in a large quantity of water it becomes red, owing to the formation of a hydrated salt, which can be obtained in crystals by the cautious evaporation of the solution. This salt forms

the basis of one of the so-called sympathetic inks. Characters written on paper with a dilute solution are almost invisible on drying on account of the feeble tinctorial power of the hydrated salt; on gently heating the paper the salt is dehydrated, and the writing becomes blue and is rendered easily visible. On allowing the paper to absorb moisture from the air, the salt again takes up water and passes into the hydrated condition, when it again becomes invisible. Magnesium platino-cyanide may be obtained in fine large crystals of a deep red colour when viewed by transmitted light; when seen by reflected light the sides of the crystals are of a golden green, and their extremities of a deep purple colour. The crystals contain seven atoms of water, and give a nearly colourless solution. When heated to 50° they part with one atom of water, and become of a yellow colour. At 100° the salt becomes white by further loss of four atoms of water: at 200° it is rendered anhydrous, and its colour again changes to yellow. If a portion of the dehydrated salt be placed on the powdered red salt it rapidly abstracts water from the latter, and a white ring or layer is formed between two yellow borders, one of which consists of the anhydrous salt, and the other of the perhydrated salt. (Hadow.)

The water of crystallization in salts is held with varying tenacities. Some salts, like sodium carbonate, give up the greater portion of their water to the air at the ordinary temperature, whilst others, like copper sulphate, require to be heated. Some salts retain one portion of their water with greater tenacity than another; thus, copper sulphate loses four atoms at 100° , but requires prolonged exposure to a temperature of 200° before it parts with the remaining quantity. Thus, too, potash-alum, $\text{Al}_2\text{K}_24\text{SO}_4 + 24\text{H}_2\text{O}$, gives off ten atoms of water at 100° , ten atoms more at 120° , the remainder being expelled at 200° , when the residue (known as burnt alum) is insoluble in water. So also zinc and magnesium sulphates, which have the same crystalline shape, each possessing seven atoms of water, yield six atoms at 100° , but retain the remainder up to a temperature of 240° . To denote this fact, the formula of these crystallized salts are occasionally written thus— $\text{ZnSO}_4\text{H}_2\text{O} + 6\text{H}_2\text{O}$, and $\text{MgSO}_4\text{H}_2\text{O} + 6\text{H}_2\text{O}$. The water retained in the salt is

regarded as more intimately connected with its constitution than the remaining six atoms : hence it is frequently termed *water of constitution* or *constitutional water*. Although this water requires a comparatively high temperature to effect its expulsion, it may be displaced by a molecule of another salt, and a series of double salts may be formed. Thus—



The term *water of halhydration* is sometimes used to denote this tenaciously-held water, in contradistinction to that of crystallization, which is essentially connected with the crystalline form of the salt.

Many dehydrated salts manifest a remarkable power of re-absorbing water from a moist atmosphere, and of passing back again into the hydrated condition. Thus, anhydrous copper sulphate passes in time on free exposure to the air into the hydrated salt, changing in colour from white to greenish blue. It sometimes happens that the affinity of the salt for water, as in the case of calcium chloride, is so intense that it is able to absorb it in sufficient quantity to liquefy or *deliquesce*. Advantage is taken of this property of certain salts in order to remove water from gases or liquids. Alcohol is dehydrated by agitating it with anhydrous copper sulphate, and gases are freed from moisture by means of calcium chloride.

It is not yet satisfactorily determined whether hydrated salts exist in solution in combination with their water, or whether they combine with this water only at the moment of crystallization. The experiments of Wüllner on the vapour tensions of saline solutions (*infra*) appear to indicate that the greater number of hydrated salts, when in solution, act in diminishing the vapour-tension of the liquid exactly as anhydrous salts; and, therefore, that it is only in the moment of crystallization that the water combines with the salt. The remarkable changes of colour which certain saline solutions experience on being heated—*e. g.*, the chlorides of cobalt and copper—may, however, be adduced as an argument to the contrary.*

* Compare Rüdorff *Pogg. Ann.*, cxlv. 599. *Chem. Soc. Journ.*, Sept., 1872.

50. Relations of Water to Heat.—An intimate knowledge of the relations of water to heat is of primary importance to the chemist. Water, under ordinary conditions, when cooled, contracts, and becomes solid at 0° : when heated, it expands, and at 100° it boils. Let us, however, examine the action of heat upon water a little more particularly. Let us suppose that we have constructed a water-thermometer, with a bulb of great capacity, by taking a large flask, say of 1,000 c.c. capacity, filling it completely with water at the ordinary temperature, and inserting into the neck of it, through a tightly fitting cork, a long narrow tube. We place our water-thermometer in a room, the temperature of which is maintained below 0° . The water in the flask immediately commences to part with its heat to the air of the room, and contracts in bulk as it cools; this contraction is rendered evident by the recession of the liquid in the tube. After a certain time, however, the liquid is observed no longer to contract; its volume apparently becomes stationary for a moment, after which it again *expands*, until it is cooled to 0° , when it is suddenly transformed into ice, and with such a sudden increase in volume that the flask is in all probability broken. Supposing, however, that we had originally filled our thermometer with ice-cold water, and had brought it into a warm room, we should notice that as the liquid acquired heat from the room it would *contract* down to a certain point, after which, with the further increment of heat, it would again expand, until it acquired the temperature of the room. It is evident, from these observations, that when water is at a certain temperature, above its solidifying point, the abstraction or addition of heat produces exactly the same effect upon its volume. The temperature of the water when it stands lowest in the thermometer-tube is found to be 4° C. At 4° C., therefore, a given weight of water occupies least bulk; the point of *maximum density* of water is at 4° C. In this respect water is anomalous: no other liquid is found to contract when heated, and to expand on being cooled. The fact that water is most dense not immediately above its freezing points, but at some distance from that point, was re-discovered by Lefevre-Gineau in the course of the determinations required to ascertain the weight of a cubic centimetre of water—the unit of

the French system of weights.* For the reason that a given bulk of water weighs more at the temperature of 4°C . than at any other temperature, it was decided to determine the weight of the cubic centimetre of water at that point. The gram, therefore, is the weight of one cubic centimetre of water at 4°C .

The anomalous expansion of water may be illustrated in a very striking manner by means of the apparatus represented in fig. 48. It consists of a glass cylinder, pierced with two holes in its side near the top and bottom, for the insertion of thermometers. It is filled with water, and placed in a room, of which the temperature is about 0° . As the liquid cools, both thermometric columns are observed to contract; but

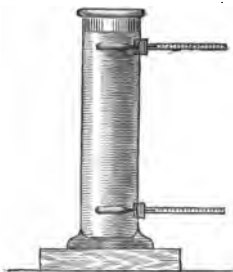


Fig. 48.

the lower one sinks faster than the other, until it reaches the point of 4°C ., when it remains stationary, whilst the upper one sinks continually to 0° , when ice begins to form on the surface of the liquid. This clearly shows that water at 4° is denser than water at a temperature below 4° . The principle of this apparatus, which was devised and employed by Hope, has also been made use of by Joule to determine the point of maximum density of water. Joule's apparatus resembled that seen in fig. 49. It consisted of two cylindrical vessels, each 1.4 metres high, and 15 centimetres in diameter, joined below by a wide tube furnished with a stop-cock, and connected above by a little channel. The apparatus was filled with water above the level of the channel, in which was placed a light bulb or gravity-bead, to indicate by its motion the direction of the flow of water from one vessel to the other. In order

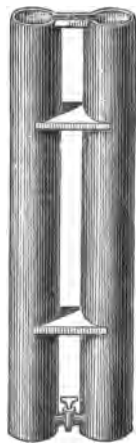


Fig. 49.

* The fact appears to have been first observed by the members of the Academia del Cimento, in the seventeenth century.

to make an observation, the cock was closed, a slight difference in the temperature of the water in each column was brought about, and, after agitation, the temperature of each mass of water was accurately determined, and the cock

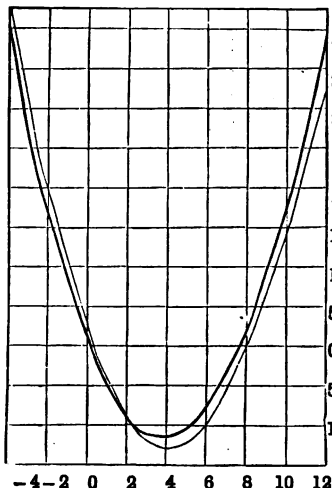


Fig. 50.

was confirmed by the experiments of Despretz, and of Plücker and Geissler, whose results, from -4° to $+12^{\circ}$, are graphically represented in fig. 50. The thick line indicates the observations of Plücker and Geissler, the thin line those of Despretz. The abscissæ represents the degrees of temperature, and the ordinates the expansions expressed in parts of a million at 0° .

$^{\circ}\text{C.}$	Despretz.	Plücker & Geissler.
-4	1,000,425	1,000,400
-2	1,000,200	1,000,175
0	1,000,000	1,000,000
2	999,915	999,915
4	999,870	999,888
6	999,900	999,925
8	1,000,000	1,000,025
10	1,000,140	1,000,175
12	1,000,340	1,000,390

These curves, especially that of Despretz, show that the expansion caused by a given decrement of temperature below the point of maximum density is perceptibly greater than that effected by an equal rise of temperature above that point. This result has been confirmed by the later observations of Pierre and Rossetti; 999,871 volumes of water at 4° become 1,003,738 volumes at - 15°, and 1,002,276 volumes at 23°. The following table, giving the means of the independent observations of Despretz, Pierre, and Kopp, shows the rate of expansion of water between 3°.945 and 24°—

t°.	V.	t°.	V.	t°.	V.
3.945	1.000000	11	1.000356	18	1.001353
5	1.000008	12	1.000463	19	1.001541
6	1.000032	13	1.000578	20	1.001743
7	1.000070	14	1.000708	21	1.001952
8	1.000121	15	1.000855	22	1.002169
9	1.000186	16	1.001005	23	1.002394
10	1.000265	17	1.001176	24	1.002642

The logarithms of these means to seven places of decimals considered as integers, are represented with great accuracy by the following formula due to Prof. W. H. Miller *—

$$32.72 (t - 3.45)^2 - 0.215 - (t - 3.945)^3.$$

The above table shows that water expands more and more rapidly with the increase of temperature.

As the mean result of all the best determinations,† it appears that one volume of water at 0° becomes 1.04300 at 100°, and that one volume at 4° becomes 1.04312 volumes at 100°.

The rate of expansion of water above 100° has been determined by Mendelejeff and by Hirn; their results are em-

* See *Phil. Trans.* 1856, 790. The above table is taken from Prof. Miller's Memoir on the "Determination of the Standard Pound."

† Viz., those of Kopp, Pierre, Despretz, Hagen, Matthiessen, Weidner, and Rossetti.

bodied in the following table; they show that the liquid expands very rapidly at the higher temperatures.

°	Mendelejeff.	Hirn.	
131.0	1.0722 *	120	1.05992 †
156.8	1.1016	140	1.07949
		160	1.10149
		180	1.12678
		200	1.15900

* Volume of water at 0° = 1.

† Volume of water at 4° = 1.

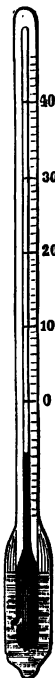
The presence of a soluble substance, as common salt or calcium chloride, in the water, renders its rate of expansion more uniform. The point of maximum density of a saline solution is always below that of water, sometimes indeed it is below its point of solidification. Rossetti has shown that the depression in the freezing point caused by dissolving common salt in the water is proportional to the amount of salt dissolved, but that the depression of the point of maximum density increases more rapidly than the proportion of salt. Some of his results are seen in the following table—

Sodium Chloride in 100 pts. of water.	Density at 0°.	Density at Max.	Temp. of Max. Density.	
1	1.007634	1.007666	+ 1.77	- 0.65
3	1.023530	1.023583	- 3.24	- 1.90
6	1.045975	1.046952	- 11.07	- 3.91
Sea-water (Adriatic)				
In June,	1.026699	1.026774	- 3.21	- 1.90
In November,	1.028141	1.028261	- 3.90	- 2.10

51. Freezing Point of Water.—The temperature at which ice melts is, under ordinary circumstances, constant, but under certain conditions water may be cooled below 0° without solidifying. Thus, when contained in closed vessels or in narrow tubes, in a state of perfect rest, it may be cooled to - 10° or - 15° without becoming solid; but on the slightest agitation it suddenly turns to ice, and the tempera-

ture rises to 0° . This fact was first observed by Fahrenheit in 1714. Water may most readily be cooled below its freezing point without congealing, by keeping it out of direct contact with the atmosphere. The apparatus seen in fig. 51 is intended to illustrate this phenomenon; it consists of a thermometer, the bulb of which is immersed in water contained in a little cylindrical vessel. The water is introduced through an opening at the bottom, and is made to boil briskly so as to expel the air from the vessel when the point is sealed by means of the blowpipe. The space above the water is thus freed from atmospheric air. The apparatus is now placed in snow or pounded ice until the thermometer stands at 0° , when it is transferred to a clear concentrated solution of common salt previously cooled to -8° or -10° . The temperature of the water round the bulb gradually sinks 4° or 5° below zero, but on the least agitation the liquid becomes ice, and the mercury column immediately rises to 0° . A mixture of chloroform and sweet almond oil in certain proportions possesses the same specific gravity as water; a drop of water placed in this mixture remains suspended in it, assuming a spheroidal shape and retaining the liquid condition even when cooled to -20° . If, however, the globule be touched with a piece of ice it solidifies immediately, increases in volume and becomes specifically lighter. This phenomenon is analogous to the case of a supersaturated solution of thiosulphate or acetate of sodium, which, as we have seen, may be cooled many degrees below the point at which the dissolved salt assumes the solid form without solidification ensuing. Rüdorff has made the very curious observation that, if a solution of a salt be cooled below 0° , ice or salt may be made to separate out at will, as the one or other solid is added to the cooled liquid. If a piece of ice be thrown into the liquid, ice alone separates out; but if a piece of the salt be dropped into it, only salt is thrown out of solution. If pieces of ice and of the salt are simultaneously thrown into the solution, water and salt solidify at the same time.

On account of this indefiniteness in the point at which



water becomes ice, the lower fixed point on a thermometer is always taken, not in freezing water, but in melting ice, which under ordinary circumstances liquefies at a constant temperature. The ordinary variations in atmospheric pressure are without sensible effect on the melting point of ice; but greatly increased pressures produce marked differences in lowering the melting point. Professors J. & W. Thomson have shown that the melting point of ice is lowered by about $0^{\circ}0075$ C. for every additional atmosphere of pressure. This decrease in melting point under pressure is peculiar to water, and is related to the fact that a given weight of water occupies less bulk in the liquid than in the solid condition. In the case of substances which, like sulphur or paraffin, are specifically heavier when solid than when liquid, an increase of pressure raises the melting point. Thus, Bunsen found for paraffin—

Under a pressure of 1 atmosphere,	$46^{\circ}3$	melting point.
„	85	„ $48^{\circ}9$ „
„	100	„ $49^{\circ}9$ „

Hopkins found for sulphur—

Pressure of 1 atmosphere,	$107^{\circ}0$	melting point.
„	519	„ $135^{\circ}2$ „
„	792	„ $140^{\circ}5$ „

By exposing ice, even when at a very low temperature, to an enormous pressure, we may expect to effect its liquefaction; and, in fact, the experiments of Mousson have shown that a pressure of 13,000 atmospheres will convert ice into water at a temperature of -18° . If we fill an iron bomb shell with water at 4° , and securely plug the fuse-hole, and expose the shell to a low temperature, although the temperature of the water may be several degrees below zero, ice is never formed within the shell, owing to the enormous pressure exerted by the water in its expansion. Occasionally this pressure is sufficient to drive out the plug, or to burst the shell, when the forms exhibited by the mass of ice which now projects from the crack or hole, show that this ice could only have been formed at the moment that the pressure on the liquid was removed (fig. 52.)

52. Regelation.—If we squeeze two pieces of ice together, they will adhere, and form a solid block. This phenomenon is termed *regelation*, and was first observed by Faraday. It has been ascribed to the effect of pressure in lowering the melting point of ice. The pressure on the pieces of ice causes a portion to melt at their points of contact; on removing the pressure, this water instantly freezes, and cements together the pieces of ice into a compact mass. The phenomenon of regelation has been supposed by some to play an important part in determining the motion of the immense masses of ice termed glaciers.

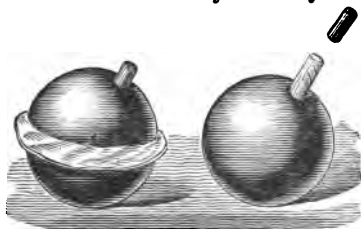


Fig. 52.

53. Expansion of Water in Freezing.—Ice floats upon water; a given weight of water therefore increases in bulk in passing from the liquid to the solid state; accordingly, the specific gravity of ice is less than that of water; the relation of their specific gravities is as 0.91674 : 1 (Bunsen). One volume of water at 0° becomes 1.09082 volumes of ice. The disruptive effect exerted by water in freezing is very great, on account of the sudden increase in the volume of the congealed water. We frequently notice in the winter months that pipes and vessels are burst by the action of freezing water. The force exerted by freezing water plays a very important effect in nature in the disintegration of rocks and minerals to form soils. All rocks absorb moisture either directly from the atmosphere, from rain, or by capillary action; when exposed to a low temperature, the enclosed water freezes, its volume increases, and it thus exerts a disruptive action upon the rock. The united effect of millions of these disruptive actions is to detach and bring down a fragment of the rock; this fragment during successive winters is again broken up into smaller fragments, the process of splitting-up being repeated, until the whole mass is reduced to a state of fine subdivision.

These considerations of the behaviour of water in the

neighbourhood of its freezing point will enable us to understand why very deep lakes never freeze. When a mass of water is exposed to a low atmospheric temperature, say below 0° , the action towards thermal equilibrium commences at the surface of the water, where it is in contact with the colder air. The water cools, therefore, and becomes specifically heavier; it sinks, and gives place to warmer and lighter water from below. This in its turn gives up its heat to the air, contracts in volume, becomes specifically heavier, and sinks. A process of circulation in the water is thus set up, until its mass is reduced to a temperature of 4° . At this point, a further abstraction of heat causes the volume of the cooled water to increase; as it cools from 4° to 0° it becomes specifically lighter; it has therefore no tendency to sink. The circulatory process ceases therefore so soon as the mass of the water acquires a uniform temperature of 4° , cooling by *convection* (as this process of transference of the water-particles is termed) is at an end, and any further reduction of temperature is brought about by *conduction*. Water, however, is such a bad conductor of heat, that if its mass is very considerable in proportion to its surface, as it is in a deep lake, the duration of the cold atmosphere is never sufficient to bring about the reduction of the whole, even to the uniform temperature of 4° . Even supposing that the upper layer becomes reduced to 0° , it will take a considerable time before the contiguous strata become reduced to the same temperature; and, accordingly, the formation of ice must take place very slowly.

Let us consider what would be the effect if water did not possess this anomalous point of maximum density, and if ice were not specifically lighter than water. In contact with a colder atmosphere, cooling by convection would go on in the manner above described, and the heavier water would sink, and in time the temperature of the mass would become reduced to 0° ; ice would first form at the upper surface, in contact with the colder air, and would sink to the bottom; and, if the cold continued, the water would be gradually solidified. But, supposing that the cold was not of sufficient duration to turn the whole mass of the water into ice, we should have a condition of things exactly analogous to that

in the experiment described on p. 99. The masses of ice at the bottom could only be melted by the process of conduc-

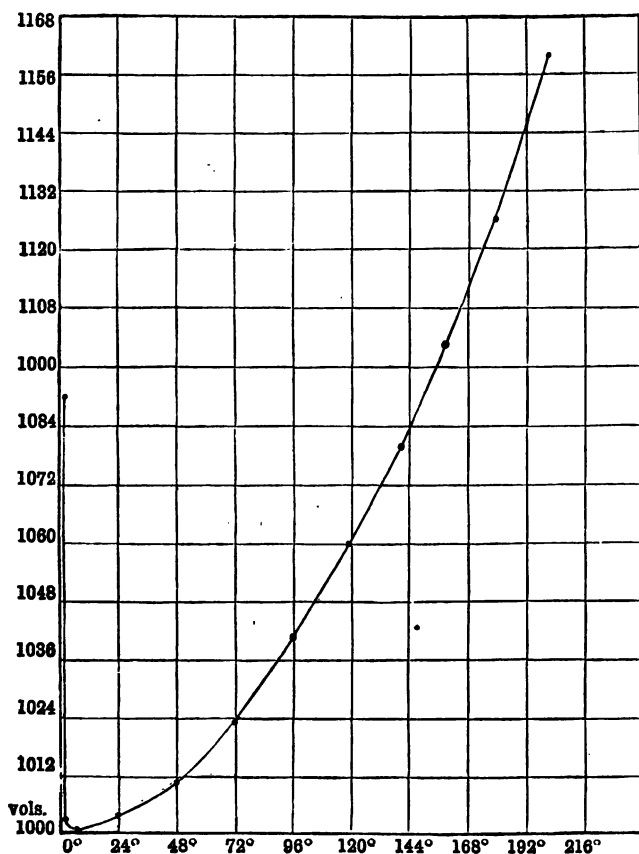


Fig. 53.

tion. As the summer air warmed the water at the surface, it would have no tendency to sink, for as it increased in

temperature it would become specifically lighter, and the duration of the summer would be insufficient to effect the liquefaction of the ice; our climate would become arctic in its character; and our lakes and rivers could not fulfil their greatest use, namely, the preservation and sustenance of a large portion of the animal kingdom.

Fig. 53 gives a graphical representation of the changes of volume experienced by water on being heated from the solid state at 0° up to 200° . The abscissæ indicate the temperatures, and the ordinates the corresponding volumes, the volume at the maximum density being 1000.

54. Latent Heat of Water.—If we take a kilogram of water at 80° C., and a kilogram of water at 0° C., and mix them together, we obtain two kilograms of water having a mean temperature of 40° . If, now, we mix a kilogram of water at 80° with a kilogram of ice or snow at 0° , we in like manner obtain two kilograms of water; *but its temperature is not 40° , it is exactly 0° .* All the heat which the kilogram of water at 80° has given out in cooling from 80° to 0° , has completely disappeared—that is, it is no longer recognizable by the thermometer. This amount of heat has been sufficient, however, to convert ice or snow at 0° into water at 0° ; in other words, the heat has been used in doing the work of converting solid water into liquid water. To denote this heat, which is thus used up, and apparently becomes hidden, the term *latent heat* has been invented. In order to compare different quantities of heat, it is necessary to adopt some distinct quantity as our unit. It has been agreed, therefore, to take as the unit of heat *that amount of heat which is required to raise 1 kilogram of water from 0° to 1° C.* Now, in the kilogram of water at 80° , there are 80 of these *heat-units*, or *thermal units*, as they are sometimes termed; hence we see that it takes 80 thermal units to convert ice or snow at 0° into water at 0° . Accordingly, the *latent heat of fusion of water is said to be 80 thermal units.*

The determination of the latent heat of fusion of water has been frequently made the subject of rigorous experiment. The method adopted by Regnault was as follows:—In a certain space, the temperature of which was not far removed from 0° , was placed a weighed quantity of water of a known

temperature. A quantity of snow was placed in a little wire-work basket, and its temperature was accurately ascertained by means of a thermometer. The basket and snow were plunged into the water, and agitated until the snow was melted, when the temperature of the whole was again ascertained. On weighing the water at the termination of the experiment, its increase in weight gave the amount of snow added. The actual numbers of one of Regnault's determinations may serve to show how the latent heat of fusion of water may be calculated from the results of these observations. The weight of water originally employed was 462.2 grams; at the end of the experiment it was 512.7 grams: accordingly, 50.5 grams of snow had been mixed with the water. The initial temperature of the water was $16^{\circ}.12$; that of the snow was $-0^{\circ}.32$; the final temperature of the mixture was $6^{\circ}.78$: accordingly, the water had been cooled through $16^{\circ}.12 - 6^{\circ}.78 = 9^{\circ}.34$. The quantity of heat given up by the water was therefore $462.2 \times 9.34 = 4317$ thermal units. But this amount of heat had been used up in converting the 50.5 grams of snow into water, and in raising the temperature from $-0^{\circ}.32$ to $6^{\circ}.78$ —that is, through $7^{\circ}.1$. To raise this amount of water to this temperature, we should need $50.5 \times 7.1 = 358$ thermal units. Accordingly, the amount of heat required to melt the snow would be $4317 - 358 = 3959$ thermal units. If 50.5 grams of snow required 3959 thermal units, 1 gram would need $\frac{3959}{50.5} = 78.5$ thermal units. Hence 78.5 is the uncorrected value of the latent heat of fusion of water. After making all the necessary corrections, this number becomes 79.2; and as the mean of several experiments made in the above manner, Regnault found 79.24 for the value of the latent heat of fusion of water. This latent heat is again given out when the water solidifies, although under ordinary circumstances there is no perceptible rise of temperature. As a rule, the freezing of water begins at different points at the same instant: the congealing portions give up their latent heat to the adjacent particles, which are therefore held liquid for a moment or two longer, until this evolved heat is dissipated. For this reason, we see in the freezing of water the creation of thin leaflets, or needle shaped pieces of ice, which gradually increase in size,

and push their way into the midst of the still liquid mass. The latent heat is thus gradually dissipated: on this account the water, when cooled down to 0° , does not instantaneously solidify.

We have already had several manifestations of this evolution of heat in the transition from the liquid to the solid condition. Thus, when the supersaturated solutions of sodium acetate, sulphate, or thiosulphate, were made to crystallize, a considerable development of heat was manifested. If gypsum be heated, its water of crystallization is expelled; and if it be now moistened, it becomes suddenly heated, owing in great measure to the recombination of the water, which enters into union in the solid state, and gives off its *heat of liquidity*, or latent heat. The slaking of lime is also attended with the assimilation of water, and the great evolution of heat with which the operation is attended is due in part to the change of state of the combined water.

If we set a flask containing water over a lamp, and throw into the water a few fragments of litmus or cochineal, we shall be able to observe the manner in which the mass of the water becomes heated. We notice that those portions of the liquid nearest to the source of heat rapidly ascend to the surface, and, arriving there, appear to fall over and descend, and again ascend on coming into contact with the heated surface, their motion being rendered evident as they become mixed with the colouring matter of the litmus or cochineal, and this process is repeated until the mass of the water appears to be in rapid circulation. The effect of heat on water is to expand its volume, and to render it specifically lighter; it accordingly rises from the heated surface, giving place to colder and heavier water. This in its turn becomes heated and ascends, and other particles of water flow into its place. In this manner heat is carried among the other particles, until the whole appears to be uniformly heated. The water thus becomes heated by convection. If we place a thermometer in the heated liquid, we notice that the mercury continues to ascend, until it reaches a certain point, when it remains stationary; bubbles of water-gas or steam are now observed to form within the liquid, which, rising, break on the surface and agitate it, giving the liquid the well known appearance

of ebullition. The thermometer now stands at 100° , and however long we continue to heat the liquid, its temperature never exceeds 100° . Here, then, we have a disappearance of heat exactly similar to that seen in the liquefaction of ice. Heat, in fact, is being used up in converting the liquid into a gas—that is, in converting the water at 100° into steam at 100° , for if we withdraw the thermometer from the liquid, and hold it in the steam, we notice that the temperature is unchanged. We can roughly determine the latent heat of vaporization by taking, say, 100 grams of ice-cold water and blowing steam into it, until the temperature is exactly 100° . The increase in the weight of the water gives us the amount of steam at 100° , which, in its condensation to water at 100° , gives out heat enough to raise the cold water to 100° . We will suppose that this increase in weight was 18.6 grams. Then 18.6 grams of steam at 100° , in condensing to water at 100° , have given out sufficient heat to raise the 100 grams of cold water from 0° to 100° . But the numbers of 18.6 and 100 are in the ratios of 1 : 5.36. We can say, therefore, that the quantity of heat necessary to change a given weight of water at 100° to steam at 100° is 536 times as great as that required to heat the same weight of water from 0° to 1° .* But the quantity of heat required to raise the temperature of the unit volume of water from 0° to 1° is styled the thermal unit; hence the latent heat of the vaporization of water is 536 thermal units.

We have frequent illustrations of the fact that a substance requires more heat for its existence in the gaseous than in the liquid condition. If a draught of air impinges on us, we feel the sensation of cold: the motion of the air promotes evaporation from the surface of the skin, and in the act of evaporation the water robs the body of some fraction of its heat. The abstraction of sensible heat on evaporation may be shown in many ways. If we pour a few drops of ether on the hand, we experience a sensation of cold, owing to the rapidity of the evaporation. By using a larger quantity of ether, and promoting its evaporation by a rapid current of air, it is possible to lower the temperature of any portion of the body to such a degree as to cause numbness or insensi-

* This statement, although nearly, is not *absolutely* true.

bility to pain in the part—a fact first observed and acted upon by Dr. Richardson, who has proposed to use ether in this manner in surgical operations. It is a common practice in hot countries to cool water by placing it in unglazed vessels, which are sufficiently porous to allow of the transpiration of water from within to the outer surface, whence it evaporates, and so cools the vessel and its contents. If a few drops of water be poured on to a wooden block, and a thin copper disc, shaped like a watch glass, and filled with ether, be placed on the board so as to be surrounded by the water, a strong current of air from a bellows will create such rapid evaporation of the ether, and consequently such an abstraction of heat from the metal and water, that the latter is robbed of its heat of liquidity, and, accordingly, solidifies; the metal and block are cemented together by the ice. Some liquids evaporate with such rapidity that they solidify; thus, when liquid carbon dioxide is caused to evaporate quickly, a portion of the liquefied gas freezes.

55. Spheroidal State.—If a few drops of water are thrown on to a hot plate, they are observed to assume a peculiar spheroidal shape, and to acquire a rapid oscillatory motion. Although the plate may be heated much above its boiling point, the water never enters into ebullition, and its volume decreases with comparative slowness. If, however, the source of heat be removed, the water, little by little, begins to boil, and at last with such rapidity, that it disappears in a momentary burst of steam. This phenomenon, which was first observed by Leidenfrost, has been accurately investigated by Boutigny, who has shown that the same effect may be produced by other liquids than water. By dropping ether on to heated water, the former liquid may be made to assume the spheroidal condition. Boutigny has proved that in all these cases the liquid is not in direct contact with the heated surface: between the water and the heated plate is a film of aqueous vapour, on which the spheroid of water rests as on an elastic cushion. Owing to the badly conducting nature of the intervening layer of vapour, the drop rarely becomes heated to the boiling point; evaporation therefore occurs only from its surface. Colley has recently re-investigated the phenomenon, and he finds

that the temperature of the spheroid varies from 90° to 100° , according to the temperature of the plate and the size of the spheroid; and that the space between the lower surface of the spheroid and the plate is, for small drops of 1 to 1.5 grams, from 0.15 to 0.25 m.m. A liquid wets the side of the vessel in which it is contained, for the reason that the adhesion between the material of the vessel and the liquid is greater than the cohesion of the liquid particles among themselves. Both the adhesion and cohesion decrease with increase of temperature; but, under ordinary circumstances, when a heated liquid, like water, is in contact with a surface but slightly hotter than itself, the force of adhesion is still greater than that of cohesion, and, accordingly, the liquid still wets the surface. If, however, the surface is far more strongly heated than the liquid, the adhesion rapidly diminishes, until at a certain point the cohesive force preponderates; the liquid no longer wets the surface, but assumes a spheroidal form (Buff).*

If a quantity of liquid sulphur dioxide be poured into platinum crucible heated to bright redness, it will assume the spheroidal state, like any other liquid. Sulphur dioxide boils at -10° ; and so long as it remains liquid, its temperature does not exceed that point under the circumstances of the experiment. If, therefore, we pour a small quantity of water into the red hot crucible, it will instantly be converted into ice—the rapidly evaporating sulphur dioxide robs it of its heat of liquidity.

By using a mixture of solid carbon dioxide and ether, Faraday succeeded in solidifying mercury, which freezes at -40° , in an ignited crucible. The mixture of solid carbon dioxide and ether, contained in a wide-mouthed test-tube held by a wire handle, was poured into the glowing crucible. A small platinum crucible, half filled with mercury, and also held by a wire handle, was then quickly inserted into the mixture of carbon dioxide and ether. In a few seconds the mercury was solidified, and the small crucible could be withdrawn and inverted without any of the metal flowing out.

56. Tension of Aqueous Vapour.—Water constantly gives off steam or vapour at all temperatures. If we expose a glass of water to the air, we find after a time that the whole of the

* *Pogg. Ann.*, 1871, 125.

water will have disappeared, or, as it is termed, will have evaporated. For a long time it was supposed that the air had the power of dissolving water, as water has the power of dissolving salt. It is very easy, however, to show that the air has nothing to do with the phenomenon, for if we place a small quantity of water in the vacuum of an air-pump, we notice that the water continues to evaporate. If we fill a tube 80 centimetres in length with mercury, and invert it in a cistern of that metal, we notice, on removing the finger, that the mercury falls in the tube until it is about 760 millimetres above the level of that in the cistern. The column of mercury is balanced by the pressure of the atmosphere. If we



Fig. 54.

The method employed by Dalton to study the laws regulating this phenomenon was very simple. A modified form of his apparatus is represented in fig. 54. It consists of two barometer tubes, A and B, filled with mercury, and dipping into a quantity of the metal. The two tubes are attached to a support so that they are maintained perfectly vertical. A

now bring a drop of water into the tube it rises through the mercury column, and we notice that almost immediately it reaches the surface, the mercurial column is depressed 10, 15, or even 20 m.m. By filling another tube with mercury, inverting it and introducing into it a quantity of ether equal in weight to that of the water, we notice that a far greater depression occurs, the mercury in the tube is now only 400 m.m. above the level of the cistern. This experiment shows that the depression of the mercury is not due merely to the weight of the liquid, for equal weights of ether and water depressed the mercury 360 m.m. and 15 m.m. respectively. This power of depressing the mercury is due to the *tension* or elastic force of the vapour. We see that various vapours have very different tensions at the same temperature.

small quantity of water is brought into A; B serves to show the pressure to which the vapour in A is subject at the moment of observation. The vessel containing the tubes is filled with water, the temperature of which is adjusted to any required degree by the addition of hot or cold water to it. The temperature is determined by a thermometer suspended in the water. The difference between the levels of the two columns of mercury represents the tension of the aqueous vapour at the observed temperature. The higher the temperature of the water in the vessel, the greater is the depressing force of the vapour. Thus, at 10° , it is found to exert a depressing force equal to 9.2 m.m. of mercury; at 20° 17.4 m.m.; at 30° 31.5 m.m. By a slight modification of the apparatus it can be shown that water, even when solid, exerts a perceptible tension; thus at 0° , its vapour tension is 4.6 m.m.; at $-12^{\circ}5$ it is 1.6 m.m.; and at $-32^{\circ}8$ it is 0.3 m.m. By reason of this elastic force, exerted even at very low temperatures, we notice that snow and hoar-frost gradually disappear, although the temperature of the air may be considerably below 0° .

Regnault and Magnus have determined the tension of aqueous vapour at temperatures between -32° and 230° with great accuracy. The following table gives some of the results of their investigations:—

Temp. p.	VAPOUR-TENSION.		Temp.	VAPOUR-TENSION.	
	Magnus.	Regnault.		Magnus.	Regnault.
°	m.m.	m.m.	°	m.m.	m.m.
-20	0.916	0.927	100	760.000	760.000
-10	2.109	2.093	110	1077.261	1075.370
0	4.525	4.600	120	—	1491.280
10	9.126	9.165	130	—	2030.28
20	17.369	17.391	140	—	2717.63
30	31.602	31.548	150	—	3581.23
40	54.969	54.906	160	—	4651.62
50	91.965	91.982	170	—	5961.66
60	148.579	148.791	180	—	7546.39
70	232.606	233.093	190	—	9442.70
80	353.926	354.643	200	—	11688.96
90	524.775	525.392	210	—	14324.80

It will be noticed that, at 100° , the vapour-tension of water is exactly equal to the pressure of the atmosphere, namely, 760 m.m. But at 100° water boils. We may say, therefore, that *water boils when its vapour-tension is equivalent to the atmospheric pressure.* What is true of water in this respect is true of all liquids. The relation between the boiling-point

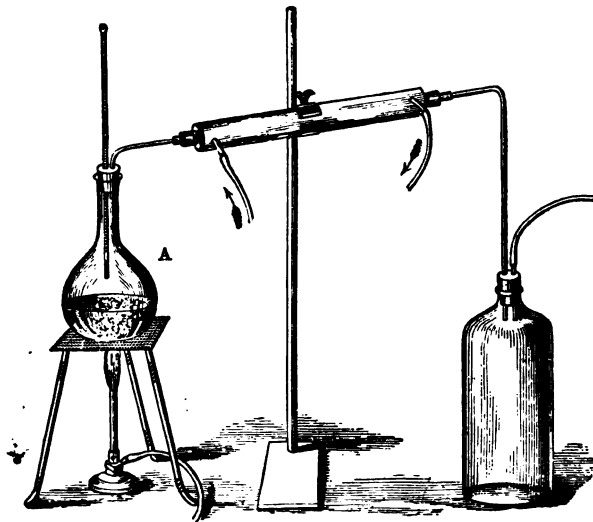


Fig. 55.

of a liquid and the pressure to which it is subject may be illustrated in a variety of ways. If we heat a quantity of water to 50° or 60° , and place it under the receiver of an air pump, and rapidly exhaust the air, we notice that the water commences to boil with as much energy as if its temperature were 100° . The apparatus represented in fig. 55 permits this relation to be determined in a very clear manner. The flask A, partially filled with water, is fitted with a caoutchouc cork, through which are inserted a thermometer and wide bent tube, leading to a condensing arrangement. The other end of the tube fits into a strong flask, which is connected with the filter-pump described on p. 100. The apparatus

is exhausted until the manometer stands, say, at 720 m.m., when, if the water be gently heated, bubbles of vapour are observed to form within it, and when the thermometer is at 30° or 35° , the water is in full ebullition, and it continues to boil regularly at this temperature so long as the diminished pressure is maintained. By allowing a little air to flow into the apparatus, the mercury in the manometer of course falls; ebullition at once ceases, and the liquid requires to be heated to a higher temperature before it recommences to boil. This temperature depends upon the pressure which the manometer now shows to be within the apparatus. So long as this increased pressure is maintained, the liquid boils regularly at a constant but higher temperature. The relation between the pressure and boiling point may be also illustrated by the familiar experiment of making water boil by placing it in contact with ice. A quantity of water in a flask is made to boil briskly, so as to expel all the air, and as the steam is rushing out, the flask is closed by a well-fitting caoutchouc cork. On removing the lamp, and inverting the flask, the water is seen to continue in slow and intermittent ebullition. This may be increased by blowing on the glass, and be restored to full energy if a piece of ice be placed on the bottom of the flask. By cooling the glass, a portion of the steam condenses; this no longer exerts a tension or pressure on the surface of the liquid, and the water recommences to boil under the diminished pressure. If the ice be removed, the ebullition ceases after a time, on account of the production of fresh vapour, which, by its tension, prevents the liquid boiling at the temperature which it possesses; but, on replacing the ice, a portion of this vapour is recondensed, the pressure is again diminished, and the liquid again enters into ebullition.

As the pressure of the atmosphere is continually changing, it is obvious that water cannot boil invariably at 100° : it boils only at this temperature when the pressure is 760 m.m. Under a pressure of 733 m.m., water boils at 99° ; under a pressure of 746.5 m.m., it boils at $99^{\circ}.5$; and under a pressure of 782 m.m., it boils at $100^{\circ}.8$. A difference of 27 m.m. in atmospheric pressure causes a difference of about 1° in the temperature at which water boils. We see therefore how important it is in graduating a thermometer to notice the height of the

barometer at the time the upper fixed point is determined; for, if the pressure is only 733 m.m., the true temperature of the steam would be 99° , and therefore the space between the freezing and boiling points would have to be divided into 99 instead of 100 equal parts. And since all places in the world are not under equal pressures of atmosphere, an elevated place like Quito, which is 2907 metres above the sea-level, cannot have the same weight of atmosphere pressing on it as London, which is only a few metres above the sea. The height of the barometer at Quito is only about 530 m.m.; accordingly water boils there at $90^{\circ}\cdot 1$. On the summit of Mont Blanc, at a height of 4772 metres, and where the atmospheric pressure is only 417 m.m., water boils at 84° , a temperature at which its vapour tension is equivalent to 417 m.m. By determining the temperature at which water boils at a given locality, we can estimate its height; instruments specially adapted to this purpose are termed *hypsometric* thermometers, from *ὑψος*, height, and *μέτρον*, a measure.

We have already described the method of determining the boiling point of a liquid (see p. 35); we now see that, in addition to the corrections enumerated, it is necessary to add another for variation in atmospheric pressure. The mean height of the barometer at the sea's level, viz. 760 m.m., is taken as the standard of pressure; and as the vapour tension of only a few liquids is known, it is usually assumed that, for small limits of barometric change, a difference of 2·7 m.m. is equivalent to $0^{\circ}\cdot 1$ C. Under ordinary circumstances, the error caused by the fact that various liquids have very different vapour tensions for the same interval of temperature is very small.

Many other circumstances, in addition to external pressure, modify the boiling point of a liquid: its internal pressure is not without influence. If we attempted to boil a column of water 32 feet in length, we should find that a temperature of 121° would be required before bubbles of steam would form at the bottom. The nature of the vessel also has considerable influence on the boiling point. If pure water be heated for some time in a perfectly clean flask, its temperature will frequently rise to 105° or 110° without any sign of ebullition appearing. In a moment, however, an explosive

burst of steam occurs (sometimes with such violence that the flask is shattered to pieces), and the temperature of the liquid sinks to 100° . This boiling by *succussion*, as it is termed, is seldom seen in metallic vessels, or when the liquid is in contact with metal; in order therefore to secure regular ebullition, it is customary to throw in a few scraps of platinum foil into the liquid. Indeed, any surface on which bubbles of vapour can collect serves to prevent irregular boiling; jagged fragments of quartz, pieces of glass, &c., may also be used. The presence of air or dissolved gas in the liquid also serves to promote regular ebullition; a small stream of air bubbles drawn through the heated liquid is found to be very efficacious.

The presence of soluble matter in it also influences the boiling point of a liquid. The following table gives the boiling points of certain saturated solutions:—

	°C.	Grams of Salt to 100 Grams of Water.
Sodium Carbonate,.....	104.6	48.5
Sodium Chloride,.....	108.4	41.2
Potassium Nitrate,.....	115.9	335.1
Sodium Nitrate,	121.0	224.8
Potassium Carbonate,.....	133.0	205.0
Calcium Chloride,.....	179.5	325.0

A thermometer placed in the steam of such boiling solutions always indicates a temperature of 100° , when the barometer is at 760 m.m. Regnault has shown, however, that a thermometer, surrounded with the steam from saline solutions, cannot possibly give the true temperature of the vapour, for the reason that condensed water covers the bulb of the instrument: this boils off the surface of the bulb, and of course gives the temperature of 100° , the boiling point of pure water. Magnus has proved that this explanation is the true one, for when special pains are taken to prevent the condensation of the water on the bulb, the thermometer acquires the temperature of the saline solution.

Mr. Spence has made the remarkable observation that, if steam at 100° be blown into a concentrated solution of sodium nitrate, the saline liquid acquires the temperature at which it ordinarily boils, viz., $121^{\circ}.0$.

Under certain circumstances water may be heated under the

ordinary atmospheric pressure far above 100° without entering into ebullition. When heated in sealed tubes, free from air, it may be raised to 150° without boiling. A certain mixture of oil of cloves and olive oil possesses the same specific gravity as water; when water is dropped into such a mixture it takes a spherical form and swims beneath the surface. The temperature of the oils may be raised even to 170° without the water boiling, but if the superheated globules come in contact with the sides of the vessel, or if they be touched with a glass rod, they boil with explosive violence.

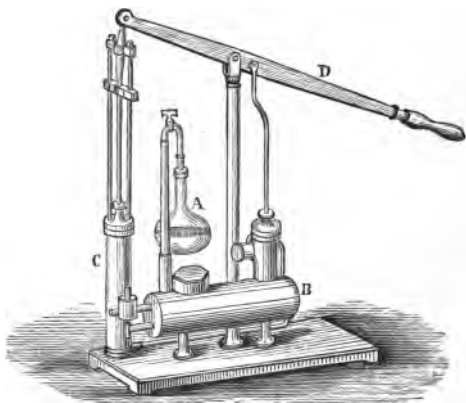


Fig. 56.

It is possible to boil water at a low temperature, and with such rapidity that the liquid portion freezes. A few drops of water placed on some badly conducting surface, and held over concentrated sulphuric acid in the vacuum of an air-pump, may be rendered solid in the course of a few minutes. This principle has been applied by M. Carré in the construction of ice-making machines. His apparatus is represented in fig. 56. The water to be frozen is placed in the flask, A, which is connected with the reservoir, B, containing concentrated sulphuric acid. On exhausting the air within the flask by means of the pump, C, worked by the lever, D, the water evaporates at a greatly increased rate, but as fast as the vapour is generated it is absorbed by the sulphuric

acid. In consequence of the diminished pressure, the water enters into ebullition, and the abstraction of heat is so great that the still liquid portion congeals. The cryophorus of Wollaston, seen in fig. 57, may be made to illustrate the same phenomenon. It consists of two glass bulbs connected together by a wide tube, one of which contains water. The space above the water is perfectly free from air, this having been expelled by boiling the water before the end of the apparatus was closed. The whole of the water is brought into the bulb, A, and the empty bulb is placed in a freezing mixture contained in a beaker. In a few minutes the water in A is seen to boil, and immediately afterwards to become frozen. The vapour rising from the surface of the water in A is so rapidly condensed, that under the diminished pressure the water boils, and robs the non-vaporizing portion of so much heat that it is unable to maintain its liquid condition, and accordingly changes to ice.



Fig. 57.

57. Natural Water.—When water is precipitated on the earth's surface in the form of rain, it permeates it to a depth more or less considerable, dependent upon the nature of the strata through which it has to make its way. When it meets with an impervious stratum it there accumulates until, finding a fissure, it is driven up to the surface as a spring. In consequence of the remarkable solvent power of water, it takes into solution portions of the earth with which it comes in contact. Hence, when once precipitated on the earth's surface, water is no longer pure. Natural waters may conveniently be classified under the heads of rain, spring, river, and sea water.

58. Rain water is the purest form of natural water. When collected in vessels upon which it exerts no solvent action, it is merely contaminated with the few impurities which it may have derived from the atmosphere in its downward passage.

59. Spring water invariably contains more soluble matter than rain water in consequence of its having been in contact with the earth. The general character of the dissolved sub-

stances in spring water is uniform; the differences are in amount and not in kind. The substances generally present are the sulphates, carbonates, chlorides, sulphides, and silicates of magnesium, calcium, potassium, sodium, manganese, and iron. These bodies are held in solution, partly by the peculiar solvent action of the water, and partly by the aid of dissolved carbonic acid. In addition to these saline bodies, we find organic matter and various gases—viz., oxygen and nitrogen, carbon dioxide, and, more rarely, sulphuretted hydrogen. When a spring water is so highly charged with gaseous or saline matter that it becomes unfit for economic use, it is classed under the category of *mineral waters*. Such waters are often highly prized for their supposed medicinal virtues.

Great disparities exist in the depths from which springs rise. Natural or artesian wells have been sunk to a depth of 850 metres;* and it is probable that many mineral waters rise from even greater depths than this. Great variations exist also in the temperature of spring waters; some are only a few degrees above the freezing point, whilst others are extremely hot, like the Sprüdel spring at Carlsbad in Bohemia, which has a temperature of 75°. There is an intimate connection between the depth from which a spring rises and its temperature; the deepest springs are generally the hottest. Springs rising below a certain depth are often unaffected in temperature by changes of season.

The dissolved saline matter in fresh spring water varies in amount from .05 to 3 grams per litre, and the gaseous matter from one or two cubic centimetres to 70 or 100 c.c. per litre. Carbon dioxide is the most abundant gaseous constituent; indeed, in many cases the whole of the gas present in spring water consists of this substance. This carbon dioxide may be derived from subterranean processes of decomposition of mineral matter, or it may be obtained from the oxidation of organic remains in the strata through which the water percolates. Except in accidental cases, the amount of organic matter in spring water is very small. When in contact with

* The depth of the Artesian well at Rochefort, which is the deepest boring hitherto effected, is 857 metres. The temperature of this water is 41°.—*Chem. Soc. Journ.*, Dec., 1871.

decaying animal or vegetable matter water always becomes more or less contaminated with the products of decay, and its value for dietetic purposes becomes greatly impaired. Indeed, it may be asserted that water charged in any degree with the products of the decay of animal matter is prejudicial to health. Water contaminated with organic matter of animal origin invariably contains albuminoid substances and ammonia, which by oxidation become changed to nitric acid. The amounts of these substances present in the water may be regarded as the measure of its impurity.

60. **River water**, although originating from fresh water springs, invariably contains less soluble matter in a given volume than spring water. The greater portion of the water of a river is derived from surface drainage. The rapid motion of the river, by which its water is continually brought in contact with the air, tends to throw out of solution the magnesium and calcium carbonates, which are held in solution by dissolved carbon dioxide. The soluble matter in river water seldom exceeds 0.5 gram per litre, and in the generality of cases, and especially in that of rivers flowing over rocks, it is very much less than this amount. The amount of organic matter in river water is invariably greater than in spring water on account of the large amount of surface drainage which finds its way into rivers. Streams flowing through richly cultivated land, or in contact with humus or decaying vegetable matter, are frequently tinged with a more or less brown or red colour. The streams flowing through tropical forests are often saturated with this colouring matter derived from decaying leaves, and are of a deep claret colour. River water has seldom the clear sparkling appearance of good spring water, as it lacks the thorough aeration and filtration which the latter has experienced. The quantity of suspended matter in the larger rivers especially is very great. Thus, in the Thames, it amounts to about 0.2 gram per litre, whilst in the Mississippi it is 0.8 gram. The amount of the earth thus continually washed into the sea by rivers is enormous. The Amazon, at its mouth, is 70 miles wide, and has a mean depth of about 30 feet; its sectional area therefore would be about 11,100,000 square feet. Supposing that it flows at its mouth at the mean velocity of

2½ miles per hour, and that it contains as a mean amount .03 gram of suspended matter per litre, it may be readily calculated that the Amazon discharges 1,870 tons of solid matter per minute, or in round numbers, 980 million tons per year.

Lake water manifests very wide differences in composition. Some lakes are almost as pure as the water which flows in and out of them; others, like the Dead Sea and the Soda Lakes of Egypt, Mexico, &c., which appear to have no outlet, are strongly impregnated with saline matter.

The following table, giving the composition of various spring, river, and lake waters, shows the essential differences in the nature of these varieties of natural water. The numbers give the amount of the several constituents in 1,000 grams of the water.

	I.	II.	III.	IV.	V.
Calcium,.....	0·0097	0·4936	0·0181	·0019	9·0000
Magnesium,.....	—	0·1987	·0047	·0008	19·8834
Sodium,.....	·0074	4·9404	·0029	—	47·9180
Potassium,.....	—	·4797	—	—	6·3851
Ammonium,.....	—	—	—	—	·0180
Alumina,.....	—	—	—	·0014	·1534
Ferric Oxide,.....	—	—	·0020	—	·0117
Manganese Oxide,.....	—	—	—	—	·0258
Carbonic Acid (CO ₂),.....	—	·1048	·0313	·0017	—
Sulphuric Acid (SO ₄),.....	·0280	·0182	·0079	·0056	·4790
Chlorine,.....	·0079	9·1874	·0083	·0047	154·4420
Bromine,.....	—	—	—	—	2·1767
Sulphur,.....	—	·0877	—	—	—
Silicon Dioxide,.....	·0190	·0034	·0030	·0001	—
Organic Matter,.....	—	—	·0261	·0114	0·6173
Total Solid Matter obtained on Evaporation, }	0·080	15·478	0·1161	·0283	240·4833

I. Ben Rhydding, Yorkshire.
 II. Old Sulphur Well, Harrogate.
 III. River Clyde, above Glasgow.

IV. Loch Katrine, Perthshire.
 V. Dead Sea.

61. Sea water is essentially a mineral water belonging to the chlorinated alkaline class, sodium chloride being its chief constituent. The amount of solid matter in the water of the ocean far away from land is remarkably constant: the mean quantity is about 35·976 grams per 1,000 grams of sea water, and its average specific gravity is 1·02975 at 0°. At the poles, however, the proportion of saline matter is somewhat smaller, on account of the large quantity of fresh-water which is produced by the melting of the icebergs; on the other hand, at the equator the proportion is larger, by reason of the rapid evaporation of the water in the tropical regions. Near the land the amount is generally below the mean quantity, from the influx of river water. In inland seas, where the water carried off by evaporation is greater than that brought down by rivers, it is observed that the proportion of solid matter is often considerably above the average amount: thus, in the Mediterranean, it is about 40 grams per 1,000 of sea water. In process of time the water of the Mediterranean would become as concentrated as that of the Dead Sea, were it not for the strong currents which pass in and out, to and from the ocean, through the Straits of Gibraltar.

The following table shows the composition of the water of the Irish Sea, collected in winter. (Sp. gr. 1·02721 at 0°).

Water,.....	966·14054
Saline Matter, consisting of—	
Sodium Chloride,.....	26·43918
Potassium Chloride,.....	0·74619
Magnesium Bromide,.....	0·07052
Magnesium Chloride,.....	3·15083
Magnesium Sulphate,.....	2·06608
Magnesium Carbonate,.....	traces.
Calcium Sulphate,.....	1·33158
Calcium Carbonate,.....	0·04754
Lithium Chloride,.....	traces.
Ammonium Chloride,.....	0·00044
Magnesium Nitrate,.....	0·00207
Silicon Dioxide,.....	traces.
Ferrous Carbonate,.....	0·00503
	<hr/>
	33·85946
	<hr/>
	1000·00000

In summer, owing to greater evaporation, and to the diminished influx of fresh water, the proportion of saline

matter in the Irish Sea slightly increases: thus, in the month of August, it was 34·082 grams per 1,000 grams of sea water. In addition to the substances above enumerated, we find in sea water minute quantities of fluorine and iodine (probably existent as calcium iodate), arsenic, silver, copper, lead, &c.

In all probability, the greater portion of the soluble matter present in sea water has been dissolved out of the earth by the action of rivers. The remarkable differences in the composition of river and sea water at first sight appear inconsistent with the belief that the sea is in great part concentrated river water. If we compare the relative proportions of the principal constituents of the water of the Clyde, and of the Irish Sea (calling the amount of chlorine in each case 100), we have—

	Cl.	CO ₂ .	SO ₄ .	Ca.	Mg.	Na.	SiO ₂ .
River Clyde, 100		377	95	218	57	35	36
Irish Sea,..... 100		trace.	14	2	6·5	56	trace.

It is seen that those substances which are brought down to the sea by the rivers in largest quantity, viz., the carbonic acid, lime, magnesia, and silica, are present in its water in the least proportion. These substances are exactly those needed by marine animals and plants to build up the inorganic structures of their frames. The abstraction of the earthy carbonates, and silica, from sea water is brought about by the vital processes of the organisms which exist in it.

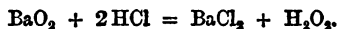
62. Water for Economic and Technical Purposes should of course be clear and free from suspended matter, especially of animal or vegetable origin. On this account, the water of springs, which experiences a process of natural filtration, is generally preferable to that of rivers, which usually contains much suspended matter, derived from surface drainage. Within certain limits, the smaller the amount of soluble matter contained in the water, the more applicable it is to economic purposes. Far more, however, depends upon the *nature* of the constituents than on their *amount*. Waters are familiarly spoken of as "hard" and "soft." These terms have reference to their behaviour with soap. Hard water contains lime and magnesia salts, which decompose soap, which is essentially an alkaline stearate, to form calcium and

magnesium stearates. These substances constitute the thin pellicle or scum seen on the surface of hard waters when treated with soap. Before it is possible to obtain a "lather" with a hard water, it is necessary to convert the whole of the calcareous and magnesian salts present in solution into insoluble stearates. Since these stearates have no detergent action, the presence of large quantities of salts of the alkaline earths in a water seriously impairs its economic value.

It is well known that some waters may be partially softened on boiling, which causes the precipitation of calcium and magnesium carbonates from their solution in carbonic acid. The hardness of other waters, however, is in no degree lessened by heating. Such waters contain sulphates of calcium and magnesium, which are held in solution by the solvent action of the water alone. Water rich in lime salts, when heated in steam boilers, tends to form incrustations on the plates, which greatly interfere with the regular and economical production of steam.

Water, to be suited to general economic purposes, should not contain more than 0·7 gram of soluble matter per litre; indeed, the better kinds of water, those, for example, which constitute the supply of our large towns, contain very much less than this amount; thus, Loch Katrine water, as supplied to Glasgow, contains 0·3 grams, and the Manchester water supply 0·7 gram per litre. The presence of *organic matter* in water exercises a much greater influence on its value for dietetic purposes than either the amount or nature of the saline constituents. It is difficult to state the precise amount of organic matter which may be contained in water used for drinking without evil resulting, since very much depends upon its specific nature. It is unequivocally established, however, that dissolved organic matter of animal origin is in certain stages of its decomposition highly injurious. The prevalence of epidemic disease has in many cases been traced to the contamination of water used for drinking with sewage or effete animal matter.

63. Hydrogen Dioxide.—This oxide of hydrogen was discovered by Thenard, who prepared it by decomposing the peroxides of the alkaline or alkaline-earth metals with a dilute acid. In the case of the barium peroxide and hydrochloric acid the reaction may be thus represented—

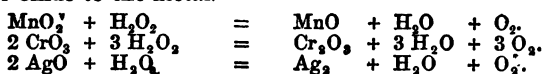


Barium peroxide may be obtained by gently heating caustic baryta (barium monoxide) in a stream of oxygen, free from moisture and carbon dioxide. An additional atom of oxygen is eagerly taken up by the monoxide, the progress of the absorption being rendered evident by a slight change in colour which gradually creeps over the heated mass. To prepare hydrogen dioxide from this compound, 12 grams of the barium peroxide in fine powder are added to a dilute and ice-cold solution of hydrochloric acid, made by adding 20 c.c. of the strong acid to 200 c.c. of water. The powder dissolves without effervescence; a quantity of dilute sulphuric acid, sufficient to precipitate the barium in solution, is now mixed with the liquid, after which 12 grams of the powdered barium peroxide are again added, and the dissolved barium again precipitated by the cautious addition of dilute sulphuric acid. This process of solution and precipitation of the barium is repeated until about 100 grams of the peroxide have been employed. The liquid must occasionally be filtered from the precipitated barium sulphate. The hydrochloric acid in solution is precipitated by agitating the liquid with silver sulphate, whereby insoluble silver chloride is formed which may be removed by filtration or decantation; the sulphuric acid now in solution may be removed by agitating the liquid with recently precipitated barium carbonate. A dilute aqueous solution of hydrogen dioxide is ultimately obtained, which may be concentrated *in vacuo* over strong sulphuric acid. For lecture illustrations hydrogen dioxide may be more conveniently prepared by adding the barium peroxide to a dilute and well cooled solution of hydrofluoric acid contained in a platinum dish. Insoluble barium fluoride is precipitated, and hydrogen dioxide passes into solution. It may also be readily obtained by adding potassium peroxide (obtained by directing a stream of air upon fused potassium contained in a

porcelain crucible) to a well cooled and moderately concentrated solution of tartaric acid, when potassium tartrate is precipitated, the hydrogen dioxide remaining in solution.

Hydrogen dioxide constitutes a remarkable example of the modifying influence of chemical action. Although the substance contains exactly the same elements as water, its properties are entirely dissimilar from that liquid. When concentrated as far as possible, it possesses a specific gravity of 1.45, and remains liquid at -30° : it may be vaporized in the vacuum of an air pump, but, when heated, it is readily decomposed. Even at ordinary temperatures it commences to part with a portion of its oxygen; and at 50° or 60° it is thrown into violent ebullition, accompanied by the production of light and heat, from the rapidity with which the oxygen is disengaged: after a time the evolution of gas ceases, and pure water remains. Concentrated hydrogen dioxide has a strong bitter taste, similar to that of tartar emetic: it whitens the tongue and thickens the saliva, and, when placed on the hand, it instantly bleaches the cuticle, and produces violent itching.

From the facility with which it gives up half its oxygen, hydrogen dioxide acts as a powerful oxidizing agent. Its reactions in this respect are analogous to those of ozone. Under certain circumstances, however, hydrogen dioxide, like ozone, may act as a reducing agent: thus, ozone and hydrogen dioxide are mutually decomposed when in contact, oxygen and water being produced: $\text{H}_2\text{O}_2 + \text{O}_3 = \text{H}_2\text{O} + 2\text{O}_2$. Similarly, hydrogen dioxide reduces manganese dioxide to the state of protoxide, chromium trioxide to sesquioxide, and silver oxide to the metal.



The reduction of chromium trioxide to the state of sesquioxide is not instantaneous; the first action of the dioxide produces by oxidation an unstable perchromic oxide of a bright blue colour, which dissolves in ether, to which it communicates its colour. This reaction affords a means of detecting hydrogen dioxide in solution: a small quantity of ether is added to the liquid, which is then mixed with a few

drops of a solution of chromic acid, when the presence of the dioxide is manifested by the formation of the deep blue colour.

It will be noticed that, in the method of preparation above described, care is taken to maintain an excess of acid in the solution; the powdered barium peroxide *is added to the acid*, and in small portions at a time. An excess of the alkaline peroxide brings about the decomposition of the hydrogen dioxide already formed. Peroxide of potassium, for example, is converted by contact with water into potassium hydroxide and hydrogen dioxide, which is immediately decomposed by the alkali with evolution of oxygen.

A solution of guaicum, mixed with blood corpuscles, or with infusion of malt, becomes blue on the addition of a solution of hydrogen dioxide; it is said that one part of the dioxide in 10,000,000 parts of water may be detected by this test. (Schönbein).

CHAPTER VI.

64. Laws of Chemical Combination.—The study of the preceding compounds, and the examples of chemical affinity contained in the foregoing pages, will serve to facilitate the explanation of certain general laws of chemical combination and decomposition, with which it is desirable that the student should make himself familiar as soon as possible.

The first is called the **Law of Constant Proportion**. It may be thus expressed:—**The same body is invariably composed of the same elements united in the same proportion.**

Potassium chlorate, for example, whatever may be its origin, is invariably made up of potassium, oxygen, and chlorine, combined together in the proportion of 39.1 parts by weight of potassium, 48 parts by weight of oxygen, and 35.5 parts by weight of chlorine. Phosphorus pentoxide, whether formed by burning phosphorus in the air, or in pure oxygen, is invariably composed of oxygen and phosphorus united in the proportion of 80 parts by weight of the former

to 62 parts of the latter. The carbon dioxide produced by the combustion of a paraffin candle in air is identical in composition with that formed by burning charcoal in oxygen, or with that given out on breathing. It is composed of 12 parts by weight of carbon united to 32 parts by weight of oxygen.

This constancy in the composition of a chemical compound enables us to express, in the form of an equation, the mode in which it is decomposed under the influence of various forces, or by the action of different reagents; it enables us also to calculate the amount of the products resulting from the decomposition of a given quantity of the substance. The law lies at the base of the principle of our methods of quantitative analysis. Thus, if we have occasion to analyze common salt (NaCl), we can combine the sodium with sulphuric acid, and the chlorine with silver; and, from the weight of the sodium sulphate and silver chloride produced, we can calculate the weights of sodium and chlorine originally contained in the salt, from the knowledge that sodium sulphate is invariably made up of 46 parts by weight of sodium, 32 parts of sulphur, and 64 parts of oxygen; and that silver chloride is always composed of 35.5 parts by weight of chlorine united to 108 parts of silver. From this uniformity in the composition of the silver chloride and of the sodium sulphate, we can make use of these compounds to determine the quantity of chlorine and of sodium, not only in sodium chloride, but also in other substances in which these elements may be separately or collectively present.

The second law of chemical combination is known as the **Law of Multiple Proportion**. It may be thus formulated:—**When an element unites with another in different proportions, the higher proportions are invariably multiples of the lowest.**

We have an instance of this law in the case of the two oxides of hydrogen, the composition of which we have thus represented:—

Hydrogen monoxide contains 2 parts of hydrogen to 16 parts of oxygen.

Hydrogen dioxide contains 2 parts of hydrogen to 16×2 , or 32 parts of oxygen.

A striking example of the law is seen in the series of the oxides of nitrogen. The composition of these substances, five in number, is as follows :—

1. Nitrogen monoxide	contains 28 parts by weight of N	to 16 parts of O.
2. Nitrogen dioxide	" 28	" " 32 "
3. Nitrogen trioxide	" 28	" " 48 "
4. Nitrogen tetroxide	" 28	" " 64 "
5. Nitrogen pentoxide	" 28	" " 80 "

The proportion of nitrogen in these compounds is the same in all, whilst that of the oxygen is increased by successive additions of 16 parts by weight. No oxide of nitrogen is, however, composed of 28 parts of nitrogen to 17 of oxygen: if the amount of oxygen is greater than 16 parts, it cannot be less than twice 16, or 32 parts: if it is greater than 32 parts, it cannot be less than three times 16, or 48 parts; and so on.

The same law holds good in every series of chemical compounds, although in some the relation is not quite so simple as in the cases above given.

The third law of chemical combination is styled the law of reciprocal proportion, and may be thus stated :—If two bodies, A and B, separately combine with a third body, C, the proportions of A and B which unite with C are measures or multiples of the proportions in which A and B combine together.

Thus, 35·5 parts of chlorine, and 127 parts of iodine, separately combine with 23·1 parts of sodium to form the compounds sodium chloride NaCl, and sodium iodide NaI. But 127 parts of iodine unite with 35·5 parts of chlorine to form the chloride of iodine ICl. Two parts of hydrogen combine with 16 parts by weight of oxygen. Hydrogen unites with chlorine in the proportion of 1 part by weight to 35·5 parts. Chlorine and oxygen combine together in the proportion of 71, *i. e.*, $35\cdot5 \times 2$ parts of the former to 16 parts of the latter. Moreover, hydrogen chlorine and oxygen are capable of existing in union together to form the compound known as *hypochlorous acid* (HClO), which is made up of 1 part of hydrogen, 35·5 parts of chlorine, and 16 parts of oxygen.

65. Atomic Hypothesis.—These laws, it must be carefully borne in mind, embody the results of experiment and

observation, and are independent of any theory of the constitution of matter. They were first distinctly enunciated by Dalton, who revived what is known as the atomic hypothesis in order to account for the facts which they express. Ancient philosophers were divided in opinion on the question of the finite or infinite divisibility of matter. The Epicureans held that matter was incapable of infinite division, and that, even if we possessed the mechanical appliances to make the minutest possible subdivision, we should at length reach a point at which the particle would resist all attempts to effect its further subdivision. These ultimate particles are called *atoms* (from *α*, *privative*; and *τεμνω*, *to cut*). Dalton was led, in 1804–8, to the resuscitation of this hypothesis in order to explain, in the first place, the difference in the composition of light carburetted hydrogen and olefiant gas, both of which gases he had analyzed and found to consist of carbon and hydrogen united in different proportions. The relation of these elements in the two compounds expressed centesimally is—

Olefiant gas,.....	Carbon 85.72	to hydrogen, 14.28.
Light carburetted hydrogen,..	„ 75.00	„ 25.00.

Dalton found, however, that these ratios might be represented in a much simpler manner. He observed that the ratio of the hydrogen to the carbon in the light carburetted hydrogen was exactly twice as great as the ratio between the same elements in the olefiant gas. In the olefiant gas the relation of carbon to hydrogen was as 6 to 1, whereas in the marsh gas it was as 6 to 2. To explain this circumstance, Dalton supposed that chemical combination consisted in the union of the small indivisible particles called *atoms*; olefiant gas he assumed to be made up of an atom of hydrogen weighing 1, united to an atom of carbon weighing 6. Since an atom is indivisible, the next higher combination of hydrogen with carbon must be 2 atoms of the hydrogen to 1 of the carbon. He thus graphically represented the composition of the two gases:—

Olefiant gas,..... (C H)

Light carburetted hydrogen, (C H H)

For reasons which will be explained hereafter, we are now of opinion that olefiant gas is more correctly represented by the formula C_2H_4 , two atoms of carbon each weighing 12, being united to 4 atoms of hydrogen each weighing 1. So also light carburetted hydrogen is now assumed to be made up of one atom of carbon weighing 12, combined with 4 atoms of hydrogen each weighing 1. But it will be observed that this manner of representing the composition of the two gases in nowise disturbs the ratios of carbon and hydrogen as given above; in the former compound it is still as 6 to 1, and in the latter as 6 to 2.

Dalton further found that the same quantity of hydrogen which combined with 6 parts by weight of carbon to form olefiant gas, also combined with 8 parts by weight of oxygen to form water. Accordingly, he represented water by the symbol

$(H\odot)$, and supposed that the atom of oxygen was 8 times

heavier than the atom of hydrogen. Extending his observations, he next discovered that the numbers which represented the proportions in which carbon and oxygen united with hydrogen, also represented the proportions in which carbon and oxygen unite among themselves. Only two oxides of carbon are known. In the first, which we call carbon monoxide, the proportion of carbon to oxygen is as 6 to 8; in the second, known as carbon dioxide, it is as 6 to twice 8, or 16.

Dalton thus represented the composition of these gases:—

Carbon monoxide,..... $(C\odot)$

Carbon dioxide,..... $(C\odot\odot)$

Since an atom is indivisible, no oxide of carbon can be formed in which the proportion of oxygen is other than a multiple of 8, when the weight of the carbon is taken as 6, and that of hydrogen as 1. We are to-day of opinion that that amount of hydrogen which unites with the 2 atoms of carbon in olefiant gas also unites with 2 atoms of oxygen, each weighing 16, to form 2 compound atoms or molecules of water, agreeing with Dalton's observation that the numbers which represent the ratios in which carbon and

oxygen unite with hydrogen, also represent the ratios in which carbon and oxygen unite with one another.

From the table of the composition of the oxides of nitrogen given above, we find that the proportion of nitrogen to oxygen in the first member of the series is as 28 to 16; this compound is made up of two atoms of nitrogen, each weighing 14, combined with an atom of oxygen weighing 16, thus,



. The next higher oxide must result from the approximation of another atom of oxygen, also weighing 16. Hence nitrogen dioxide may be represented by the symbol



, and as the result of experiment we find that the relation of the weight of the nitrogen to that of the oxygen in this body is as 28 to 32, *i. e.*, 14×2 to 16×2 . The next oxide must, in like manner, be formed by the addition of an atom of oxygen to the preceding body. Accordingly, it would be represented by the symbol (NNOOO) ;

and we actually find on analysis that it is made up of nitrogen and oxygen in the proportion of 28 parts of the one to 48 parts of the other, *i. e.*, as 14×2 to 16×3 ; and so on with the remainder of the oxides, each successive oxide being formed by the approximation of an additional atom of oxygen weighing 16. In like manner all the elements have particular numbers attached to them which are termed their atomic weights; the proportions by weight in which they combine together are always in the ratios of these numbers, or of certain multiples of them.

The foregoing laws of combining proportion are the expression of well ascertained facts, and as such admit of no question. Dalton's explanation of them, however, being based upon pure hypothesis, is not universally accepted by chemists. Davy, who objected to Dalton's doctrine, proposed to substitute the word "combining proportion" for that of "atom," and although the latter term is still in general use among chemists, it has in great measure lost its original materialistic meaning, and is used by many in an abstract sense, as expressing merely the smallest indivisible proportion by weight in which an element goes in and out of combination.

The ratios in which the various elements combine with

one another may now be considered as fixed within comparatively narrow limits. We are sure that 35.5 approximately represents the combining proportion of chlorine, when hydrogen is taken as unity. Still, as our methods of experimenting become more refined, and errors of observation are eliminated, we may come to regard 35.46 as a more correct representation of the atomic weight of chlorine than 35.50; a more rigorous analysis of water may even show that 15.96 more accurately expresses the atomic weight of oxygen than 16. But, as the student will have gleaned from the preceding paragraphs, chemists have not always been agreed to take the particular numbers given in the table on p. 16, as the relative atomic weights of the elements. Formerly the atomic weight of oxygen was held to be 8, and that of carbon 6, hydrogen being 1; to-day we are of opinion that the numbers 16 and 12 more correctly represent the atomic weights of these elements. It is necessary therefore to explain the reasons which guide chemists in the selection of one of several possible ratios as the atomic weight of an element. The selection is based partly upon chemical, and partly upon physical considerations. That particular ratio is chosen which (1.) Enables the combinations of the body to be expressed by the simplest series of formulæ, capable of illustrating their decompositions and their analogies to other compounds; and (2.) Which is in accord with its physical properties, specific volume, specific heat, isomorphism, &c. Still we must premise that it is not invariably possible to find a value which satisfies all these requirements, and consequently we are sometimes driven to select certain of them as criteria. Now, chemists are not agreed in the adoption of the criteria, for the reason that it is impossible to decide upon their relative importance. In cases of disparity some prefer to base their determination upon purely chemical considerations, such as the chemical properties of the element, the analogies and metamorphoses of its compounds, &c.; whilst others give the pre-eminence to the physical relations of the body, as, for example, its specific heat and specific volume. Accordingly, it sometimes happens that two different numerical values (which, however, have generally some simple relation to one another) are given to one and the same element.

We proceed to show how the atomic weight of the four typical elements, hydrogen, oxygen, nitrogen, and carbon, may be deduced from chemical considerations.

1. When hydrochloric acid is brought into contact with sodium, the whole of the hydrogen of the acid is expelled, and sodium chloride is formed. 36.5 parts of hydrochloric acid, made up of 35.5 parts of chlorine and 1 part of hydrogen, produce, with 23 parts of sodium, 1 part of hydrogen gas and 58.5 parts of sodium chloride, composed of 35.5 parts of chlorine and 23 parts of sodium. *The hydrogen in hydrochloric acid is indivisible*; no reaction is known in which the hydrogen is expelled in successive stages.

2. With water, however, the case is different. If sodium be thrown upon this liquid, we notice that 1 part of hydrogen will be evolved by the decomposition of 18 parts of water, and that 1 part will remain in combination with the 16 parts of oxygen and the 23 parts sodium to form sodium hydroxide, which may be obtained on evaporation. If the solid sodium hydroxide be heated with a second portion of sodium, the second moiety of the hydrogen will be expelled, and sodium monoxide will be obtained.

We notice, therefore, this striking difference in the behaviour of sodium towards hydrochloric acid and water,—that whereas in the case of water the hydrogen is expelled in two successive stages, perfectly distinct from one another, in the case of the hydrochloric acid the hydrogen is eliminated in a single stage. Hydrochloric acid is made of one indivisible part or atom of hydrogen united to 35.5 parts of chlorine; water is composed of two indivisible parts or atoms of hydrogen united to 16 parts of oxygen. This quantity of oxygen is the smallest indivisible weight of oxygen which can enter into the above reaction; accordingly, this weight of oxygen, 16, is regarded as the atomic weight of that element. A comparison of a great number of chemical reactions has served to verify this conclusion, that 16 parts is the smallest indivisible proportion of oxygen which enters into or goes out of chemical combination. We find that the quantity of oxygen in all oxidized bodies may be represented by 16, or some multiple of 16 parts; and that if the members of a series of bodies differ from one another in the amount of oxygen which they contain, the

difference amounts to 16 parts, or to some multiple of 16 parts. We have had illustrations of this fact in the case of the oxides of hydrogen and of the oxides of nitrogen; it is also evident from the composition of the following series of bodies:—

- Potassium chloride, composed of 39·1 parts of potassium and 35·5 parts of chlorine.
- Potassium hypochlorite, composed of 39·1 parts of potassium, and 35·5 parts of chlorine, and 16 parts of oxygen.
- Potassium chlorite, composed of 39·1 parts of potassium, and 35·5 parts of chlorine, and 32 parts of oxygen.
- Potassium chlorate, composed of 39·1 parts of potassium, and 35·5 parts of chlorine, and 48 parts of oxygen.
- Potassium perchlorate, composed of 39·1 parts of potassium, and 35·5 parts of chlorine, and 64 parts of oxygen.

We are not acquainted with any compounds in which the amount of oxygen is intermediate between that of any two consecutive members of the above series, nor have we any reason for believing that such will be discovered.

3. The atomic weight of nitrogen was formerly regarded as 4·67, but all chemists are now agreed to represent this weight by 14—i. e., $4·67 \times 3$; this being the smallest indivisible part of nitrogen which goes in and out of combination. We can replace the hydrogen in ammonia—the hydride of nitrogen—by thirds; that is, the quantity of hydrogen contained in ammonia may be divided into three equal parts, which can be expelled in three successive stages of a reaction. We must admit, therefore, that the molecule of ammonia must contain three indivisible proportions or atoms of hydrogen, just as we believe that the molecule of water contains two atoms of hydrogen. On heating potassium in ammonia gas a compound is formed termed *potassamine*. This substance is derived from ammonia by the replacement of one-third of the hydrogen by potassium. By continuing the action of the potassium a second and a third proportion of hydrogen may be expelled, and eventually a compound termed *tripotassamine* is formed, in which the proportion of the alkaline metal is three times as great as in the first named body. Seventeen parts of ammonia are therefore made up of 3 parts of hydrogen and 14 parts of nitrogen. This weight of nitrogen is the smallest indivisible proportion of that element which can exist. Whenever nitrogen is

liberated from, or introduced into, a chemical compound we find that the amount which reacts is invariably 14 parts by weight, or is some multiple of 14 parts.

4. Turning our attention to carbon, the atomic weight of which was formerly regarded as 6, we wish to show that this weight is more justly represented by 12. We find that the combination of carbon and hydrogen, termed *methane* or *marsh gas*, contains 4 indivisible parts or atoms of hydrogen, since we can successively replace one-fourth, one-half, three-fourths, or the whole of the hydrogen by certain other elements. Thus, with chlorine, we can obtain the following derivatives:—

Methane,	CH_4 .
Chloromethane,	CH_3Cl .
Dichloromethane,	CH_2Cl_2 .
Trichloromethane,	CHCl_3 .
Tetrachloromethane,	CCl_4 .

Sixteen parts of methane are therefore made up of 4 parts by weight of hydrogen and 12 parts of carbon. This amount of carbon—12 parts by weight—is the smallest indivisible proportion of carbon which unites with hydrogen, and also with chlorine. It is likewise the smallest quantity which unites with 16 parts by weight of oxygen, or with 14 parts of nitrogen. Moreover, we find that in a series of carbon compounds, the difference in the proportion of carbon contained in the various members may invariably be represented by 12 parts, or by some multiple of 12 parts, by weight—never by a less quantity. We are accordingly obliged to admit that the relative weight of the smallest indivisible portion, or in other words, the atomic weight of carbon, must be 12.

66. Determination of Atomic Weight from Specific Volume.—The observation of the vapour density of an element affords one of the most important means of controlling its atomic weight. We have already stated (p. 49) that if we take the weight of a given volume of hydrogen as unity, experiment shows that the weights of the same volume of the various elementary gases are expressed by the numbers we have already selected as representing their atomic weights. Thus 11.19 litres of hydrogen measured at 0° and under a pressure of 760 m.m. of mercury weigh 1 gram.; 11.19 litres

of oxygen, nitrogen, and chlorine, measured under the same conditions, weigh 16, 14, and 35.5 grams respectively. The specific gravities of the undernoted elements, when in the state of gas and measured under identical conditions of temperature and pressure, are observed to be respectively as follows:—

Hydrogen,	1	Potassium,	39.1*
Nitrogen,	14	Cadmium,	56
Phosphorus,	$15.5 = \frac{1}{2}$	Selenium,	79.5
Oxygen,	16	Bromine,	80
Sulphur,	32	Mercury,	$100 = 2\frac{1}{2}^{\circ}$
Chlorine,	35.5	Iodine,	127
Arsenic,	$37.5 = \frac{1}{2}$		

It is evident, therefore, that if, as we have every reason from chemical considerations to believe, the relative weights of the atoms of hydrogen, oxygen, nitrogen, and chlorine are respectively 1, 16, 14, and 35.5, then equal volumes of these several gases must contain the same number of atoms, when measured under identical conditions. If we assume that what is true of hydrogen, oxygen, nitrogen, and chlorine is equally true of any other element when in the state of gas, it is further evident that the determination of the specific gravity of an element when in the gaseous state may give us a means of estimating its atomic weight in cases where chemical considerations fail to indicate the precise number.

In two or three instances, however, which are quoted in the above table, it appears that the relative vapour density of the element does not agree with the number which we have preferred as representing its atomic weight. Thus the atomic volumes of phosphorus and arsenic are only one-half of that of hydrogen; in order, therefore, to make their atomic weights correspond with their atomic volumes we should have to double the commonly received numbers; P would thus become 62, and As 150. But all chemical considerations and, with this exception, every physical one, are in favour of P 31, and As 75. The atomic volume of sulphur was at one time regarded as anomalous, but later experiments have shown that when its vapour is heated sufficiently high, its

* The experiments of Messrs Dewar & Dittmar (Proc. Royal Soc., 1873), plainly indicate that the vapour density of potassium is normal.

density agrees with the number demanded by its atomic weight. At temperatures but little above its boiling point, an atomic proportion of sulphur-vapour occupies only $\frac{1}{8}$ the bulk of an atomic proportion of hydrogen under the same conditions; at 1000° , however, 32 parts by weight of sulphur and 1 part by weight of hydrogen occupy the same volume. We have already seen that the liquifiable gases in the neighbourhood of their points of condensation exhibit marked deviations from the physical laws affecting perfect gases; it is only at temperatures very remote from that at which they become liquid that they conform to the laws of Charles and Boyle. It may happen, therefore, that at temperatures higher than those at which the observations have hitherto been made, that the vapour of phosphorus and arsenic, like that of sulphur, may be found to conform to Ampère's law.

The formula of a compound substance represents the number of the elementary volumes which constitute it. Thus, the formula HCl denotes that this gas is made up of 1 vol. of hydrogen united to 1 vol. of chlorine, forming 2 vols. of hydrochloric acid gas. The formula H_2O shows, as indeed we have experimentally learned is the case, that 2 vols. of hydrogen unite with 1 vol. of oxygen to form 2 vols. of steam. So also the formula NH_3 denotes that 1 vol. of nitrogen unites with 3 vols. of hydrogen to form 2 vols. of ammonia gas. Accordingly, the specific gravities of these bodies—hydrochloric acid gas, steam, and ammonia gas—must be the halves of their atomic weights when hydrogen is taken as the unit of weight and volume. It is obvious that, if 2 vols. of hydrogen, each weighing 1, unite with 1 vol. of oxygen weighing 16, to form *two* vols. of steam, together weighing 18, then *one* vol. of steam must weigh 9; in other words, steam must be nine times heavier than hydrogen. What is true of steam is equally true of ammonia and of hydrochloric acid, which are respectively found to be 8.5 and 18.25 times heavier than hydrogen. It is true of the great majority of compound substances *that their vapour densities are the halves of their molecular weights.*

It will be also obvious that, if we know the weight of a given volume of hydrogen at a definite temperature and pressure, say of 1 litre at 0° and 760 m.m., we can readily

calculate the weight of a litre of any simple or compound gas when we know its atomic or molecular weight. In the case of a simple gas, we have only to multiply the atomic weight by the *crith*, or 0.0896, the weight in grams of 1 litre of hydrogen at 0° and 760 m.m. Thus—

1 litre of oxygen, at 0° and 760 m.m., weighs 16×0.0896
 $= 1.4336$ grams.

1 litre of nitrogen, at 0° and 760 m.m., weighs 14×0.0896
 $= 1.2544$ grams.

1 litre of chlorine, at 0° and 760 m.m., weighs 35.5×0.0896
 $= 3.1808$ grams.

To obtain the weight of a litre of compound gas, we multiply half its molecular weight by the *crith*.

Thus the molecular weight of water, H_2O , is $2 + 16$ or 18; the weight of a litre of steam, on the assumption that it could be cooled down to 0° without condensing, would be $\frac{18}{2} \times 0.0896 = 0.8064$ gram.

So, also, the molecular weight of ammonia, NH_3 , being $14 + 3$ or 17, the weight of a litre of ammonia gas is $\frac{17}{2} \times 0.0896 = 0.6708$ gram. The molecular weight of hydrochloric acid gas, HCl , is $1 + 35.5 = 36.5$; accordingly, the weight of 1 litre of this gas is $\frac{36.5}{2} \times 0.0896 = 1.6352$ grams.

Certain exceptions to this law are known, not only among the elementary bodies, but also among compound gases. In the case of the latter class of exceptions, the vapour density is *less* than corresponds to the molecular weight. When we inquire into the reason of the anomaly, we find that the exceptions, in the majority of instances, are only apparent, and may be satisfactorily accounted for by the circumstance that at the temperature required to bring them into a perfectly gaseous condition the bodies *dissociate*—that is, the complex molecule splits up into simpler compounds, which, as the temperature is lowered, recombine to form the original body. Thus, the vapour density of ammonium chloride is found to correspond to 4 vols. of hydrogen instead of 2, as demanded by theory. It has been experimentally shown that, at the temperature needed to bring the ammonium chloride into a perfectly gaseous state, it is decomposed into hydrochloric

acid and ammonia, which exist side by side in a state of mechanical mixture; 2 vols. of sal-ammoniac vapour thus expand to 2 vols. of hydrochloric acid and 2 vols. of ammonia. As the temperature is reduced, the hydrochloric acid and the ammonia recombine to form sal-ammoniac. The same phenomenon is seen in the case of sulphuric acid; at a high temperature this body dissociates into sulphuric trioxide and water, which reunite when the temperature is reduced, and again form sulphuric acid.

Since the molecules of steam, of ammonia, of hydrochloric acid, and indeed of the vast majority of compound bodies, correspond with two volumes of hydrogen, whilst the atom of an element corresponds, with very rare exceptions, with one volume, it is obvious that the amount of an element, which is strictly comparable to the molecule of a compound body, must be represented by two volumes. We regard the molecule of an element as made up of two atoms; indeed we have reason to believe that when the elements are liberated from combination their atoms assume this dual or molecular condition. The *atom* is accordingly defined to be the smallest quantity of an element which exists in combination; the *molecule* as the smallest quantity which can exist in the free state. The symbol H therefore represents the atom of hydrogen, and the symbol H_2 the molecule. We know of certain combinations of elements termed *compound radicals* which react like simple substances; these bodies also resemble the elements in so far as they occupy in the free state a bulk equal to two volumes of hydrogen, whereas in combination their volume corresponds to only half that quantity.

67. Determination of Atomic Weight from Specific Heat.—Another physical consideration of the highest moment in fixing the atomic weight of an element is based upon the circumstance first pointed out by Dulong and Petit, that all elementary atoms have the same capacity for heat. It is found by experiment that it requires equal quantities of heat to raise 32 parts by weight of sulphur, 31 parts of phosphorus, 75 parts of arsenic, and 7 parts of lithium, through the same interval of temperature. It is evident, therefore, that the product of the specific heat of an element multiplied by its atomic weight must be a constant quantity—

	Specific Heat. Atomic Weight.			
Sulphur,	0.2026	×	32	= 6.48
Phosphorus,	0.2120	×	31	= 6.57
Arsenic,	0.0814	×	75	= 6.11
Iron,	0.1138	×	56	= 6.37
Lead,	0.0314	×	207	= 6.50
Silver,	0.0570	×	108	= 6.16
Lithium,	0.9408	×	7	= 6.59

Mean, 6.40

The mean atomic heat, as the value of the product of the specific heat multiplied by the atomic weight is termed, is 6.4. The variations from the mean value are due partly to experimental errors, and partly to the impossibility of obtaining the elements in strictly comparable conditions. The hardness of the body, its crystalline or non-crystalline condition, its tendency to become softened, and to expand on being heated, all affect the amount of heat required to raise its temperature through a given interval. There is little doubt that if these disturbing influences could be removed, the law of Dulong and Petit would more correctly express the results of observation. Remarkable illustrations of the value of specific heat determinations in controlling atomic weights, are seen in the cases of the two latest discovered elements, thallium and indium. In physical properties thallium is closely allied to lead; but in certain of its compounds it exhibits near relationship to the alkaline metals. Opinions were divided, therefore, as to the particular value to be assigned to it, until it was found that the specific heat of thallium was 0.032. This number divided into 6.4, the mean atomic heat, gives 200, which points to 203.5, the number demanded by the supposition that thallium is to be classed among the group of the alkaline metals, rather than to 407, the number required by the assumption that the element is chemically related to lead. In chemical characters indium is apparently closely related to zinc, and on the basis of this relationship the value of In was considered to be 75.6, until Bunsen found the specific heat of the metal to be .0570. This number divided into 6.4 gives 112.3, which indicates that the number formerly assumed as the atomic weight must be raised to 113.4—*i. e.*, perfectly multiplied by $1\frac{1}{2}$.

Certain marked exceptions to Dulong and Petit's law occur in the cases of the undermentioned elements, the specific heats of which are all much lower than their well established atomic weights would indicate.

	Atomic Weight.
Boron,	{ Graphitic, $0.2352 \times 11 = 2.59$
	{ Crystallized, $0.2500 \times 11 = 2.75$
Carbon,	{ Wood charcoal, $0.2415 \times 12 = 2.90$
	{ Graphite, $0.2008 \times 12 = 2.41$
	{ Diamond, $0.1469 \times 12 = 1.76$
Silicon,	{ Crystallized, $0.1774 \times 28 = 4.97$
	{ Fused, $0.1750 \times 28 = 4.90$

The various allotropic modifications of these elements have therefore different specific heats; but none of the values above given agree with those demanded by Dulong and Petit's law.

Weber and, independently, Dewar, have shown that in the case of carbon the specific heat increases very rapidly with the temperature; if the specific heat were taken at very high temperatures, say in the neighbourhood of 500° , the atomic heat would in all probability more nearly correspond to the mean atomic heat of the elements, viz., 6.4 .

According to Weber the true specific heat of the diamond—that is, the quantity of heat required to raise the temperature of the unit of weight at—

0°	= 0.0947
50°	= 0.1435
100°	= 0.1905
150°	= 0.2357
200°	= 0.2791 .

The specific heat of an element is not altered when the substance enters into combination; hence the molecular heat of a compound is the sum of the atomic heats of its constituents.

This is well seen in the case of the following substances:—

	Sp. Heat.	M. Wt.
Potassium chloride, KCl	= $.1729 \times 74.5$	= 2×6.4
Sodium iodide, NaI	= $.0868 \times 149.8$	= 2×6.4
Stannous chloride, SnCl_2	= $.1016 \times 189$	= 3×6.4
Barium chloride, BaCl_2	= $.091 \times 208.3$	= 3×6.4

Owing to the difficulty of making the observations under precisely analogous conditions, the deviations from the calculated specific heats are even more numerous in the case of compound bodies than in that of the elements.

68. Determination of Atomic Weight from Isomorphism.

—The atomic weights of the elements are occasionally determined by the crystallographic relations of their compounds. Thus the fact that certain compounds of phosphorus and arsenic have the same crystalline shape as the analogously constituted compounds of nitrogen, supports the conclusion that the atomic weights of P and As are respectively 31 and 75, despite the fact that the vapour densities of these bodies seem to indicate that these numbers should be doubled. The identity of crystalline shape, that is the *isomorphism* of certain sulphur and selenium compounds, has served to establish the atomic weight of selenium and the formulæ of its compounds. The atomic weight of titanium and the formulæ of certain of its compounds have in a similar manner been controlled by the fact that stannic and titanic oxides are isomorphous. A striking confirmation of the aid which may be derived from isomorphism is seen in Roscoe's research upon vanadium and its compounds. This rare element was formerly supposed to be closely allied to chromium, and on the basis of the apparent relationship of certain chromium and vanadium compounds, its atomic weight was regarded as 67.3, until Roscoe showed that the element is a member of the nitrogen family, and possesses the atomic weight 51.3. This conclusion is in harmony with the fact which had long been known, but was hitherto inexplicable, that a certain mineral of vanadium is isomorphous with two minerals of phosphorus and arsenic. Roscoe has shown that these minerals are not only isomorphous, but that they are also similarly constituted. Still isomorphism cannot be received as an infallible guide in determining the atomic weight of an element. Thus sodium nitrate, NaNO_3 ; calc spar, CaCO_3 ; and red silver ore, Ag_3SbS_3 , are isomorphous, but these compounds are distinctly heterologous. Moreover, we frequently find that analogously constituted and closely related compounds are heteromorphous. Thus certain tellurium compounds have a different crystalline shape from the similarly constituted compounds of sulphur and selenium, and potassium nitrate does not usually assume the same crystalline form as sodium nitrate.

CHAPTER VII.

69. Nitrogen.—Symbol N; atomic weight 14; density 14.

This gas was discovered by Rutherford, in 1772. Its properties were examined more closely by Scheele and by Lavoisier; the latter demonstrated its existence in the atmosphere, and named it azote, from its incapacity to support animal life. The name Nitrogen, denoting that this element is an essential constituent of nitre, was subsequently given to the gas by Chaptal.

Nitrogen is a very abundant element. It occurs in the free state in the air, of which it constitutes four-fifths by volume, and it is emitted in large quantity from subterranean sources. In combination with oxygen it exists as nitric acid, and in combination with hydrogen, as ammonia. These compounds are very widely diffused, and play an important part in the economy of plant life. Nitrogen is an essential constituent of animal and vegetable organisms. It occurs in many minerals, and in meteorites. Mr. Huggins has shown that those singular aggregations of gases, the nebulae, consist in great part of free nitrogen gas.

70. Its Preparation.—Nitrogen may readily be obtained from the air. If a piece of phosphorus be burnt in a confined portion of air, the oxygen will be withdrawn, owing to the formation of phosphoric pentoxide. The withdrawal of the oxygen by means of phosphorus takes place even at the ordinary temperature. If a tube containing air, and standing over water, be divided into five equal parts (fig. 58), and a stick of phosphorus be introduced into it, it will be seen in a few hours that the water will have risen through one of the divisions in consequence of the absorption of the oxygen. Air may also be deprived of its oxygen by passing it over heated metallic copper, whereby cupric oxide is formed, and pure

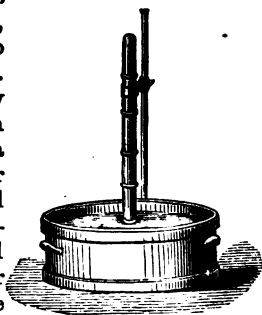
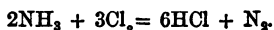


Fig. 58.

nitrogen remains. A strong solution of cupric chloride in hydrochloric acid in contact with copper turnings becomes converted into cuprous chloride. This solution absorbs oxygen from the air, and the cuprous chloride is reconverted ultimately into cupric chloride. $\text{Cu}_2\text{Cl}_2 + 2\text{HCl} + \text{O} = 2\text{CuCl}_2 + \text{H}_2\text{O}$. This reaction affords a ready method of preparing a small quantity of pure nitrogen.

It has already been stated that nitrogen is a constituent of ammonia. It may be readily liberated from its combination with hydrogen by the action of chlorine—



If a stream of chlorine gas be led into a strong solution of ammonia, nitrogen is liberated in accordance with the above reaction, and the hydrochloric acid combines with a further quantity of ammonia to form ammonium chloride—

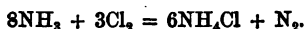


Fig. 59 represents the apparatus in which this decomposition may conveniently be effected. The chlorine is generated in

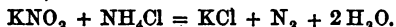


Fig. 59.

the flask *a*, and reacts upon the strong solution of ammonia contained in the bottle *b*. The tube enters *b* through a wider tube which passes through the cork and ends beneath

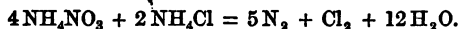
the surface of the liquid. This arrangement constitutes a safety-valve. If the ammoniacal solution should by any chance rush up the tube, it can be instantly raised from the liquid, which may thus be prevented from passing over into the flask. It is necessary, in preparing nitrogen by this method, to keep the ammonia always in excess, otherwise the chlorine reacts upon the ammonium chloride, and forms a highly explosive combination of chlorine and nitrogen.

When a solution of ammonium nitrite is heated, the salt decomposes into free nitrogen and water, $\text{NH}_4\text{NO}_2 = 2\text{H}_2\text{O} + \text{N}_2$. As this salt is somewhat difficult to prepare, it is better to heat a mixture of potassium nitrite (which is more readily obtained) and ammonium chloride—



Potassium nitrite may readily be obtained by passing the gases obtained by heating starch or arsenious acid with strong nitric acid into solution of potassium hydroxide, of specific gravity 1.38, until it acquires a distinctly acid reaction. When required for use it is heated with three times its volume of strong ammonium chloride solution.

Nitrogen may also be prepared from certain nitrates. If dry ammonium nitrate be heated with solid ammonium chloride the following reaction ensues—



The chlorine may be absorbed by passing the gas through milk of lime.

Nitrogen may be obtained from flesh or muscular fibre by heating it with dilute nitric acid. The gas produced in this reaction is always accompanied by dioxide of nitrogen, from which it may be freed by passing through a solution of ferrous sulphate.

71. Properties of Nitrogen.—Pure nitrogen is a colourless, tasteless, inodorous gas, which has resisted every attempt to effect its liquefaction. Its specific gravity is 0.972, air being 1. It is very sparingly soluble in water: 100 c.c. dissolving about 1.5 c.c. of the gas at the ordinary temperature. Under ordinary circumstances, it is incombustible, and a non-supporter of combustion: a lighted taper plunged into the gas is immediately extinguished, without

inflaming the nitrogen. Although nitrogen is, generally speaking, a very inert body, it combines with certain substances with great energy. Tungsten and titanium, when finely divided, become incandescent when projected into an atmosphere of the gas, owing to the formation of nitrides of these metals. Other methods of effecting the combination of nitrogen with oxygen, hydrogen, carbon, &c., will be described in subsequent chapters. Animals immersed in an atmosphere of nitrogen are immediately suffocated, not from any direct poisonous action of the gas, but from the absence of oxygen. It is evident that the gas cannot exert any direct injurious action, since we inhale it in large quantity at every inspiration.

72. The Atmosphere.—The word atmosphere (from *ἀτμός*, *vapour*; and *σφαῖρα*, *a sphere*), in its most extended sense, denotes the gaseous envelope surrounding any liquid or solid body. In a restricted sense, namely, that in which we now employ it, it signifies the invisible elastic fluid which surrounds the earth.

The fact that a subtle and invisible principle intimately related to life existed everywhere around him, must have been one of the earliest and most perplexing of man's impressions. Of the nature of this principle he was, of course, ignorant; but that he knew how essential it was to existence seems evident from the early use of such words as, "breath," "spirit," "ether," "air," "life"—terms which all conveyed pretty much the same idea. The earliest Greeks, we are told, deified this principle; and Anaximander, whose name is handed down to us as the first to profess any system of philosophy, taught that air was the first principle of all things.

Hesiod and Homer, who lived long before the use of letters was generally known, speak familiarly of many of the more striking properties of air. The former, in his treatise on agriculture, dwells upon the beneficial effects of winds, which Anaximander considered to be due to the rarefaction of air under the influence of heat. The ponderability of air was suspected before the time of Aristotle—indeed, this philosopher himself states that a bladder, when inflated,

is heavier than when empty and collapsed. Ctesibius, of Alexandria, and his pupil Hero, are noted for their recognition and practical application of some of the more apparent properties of the air. The former is credited with the invention of the organ, and his name is connected with a machine for propelling stones by means of air previously condensed by a syringe. Hero, who lived B.C. 200, considered that the air is composed of minute, light, and, for the most part, invisible particles. He demonstrated that the air was material: he found that, when contained in a confined space, it may be rarefied by suction, and he describes a cupping instrument which constitutes a rude form of air-pump. He treats of the vacuum, and gives reasons for its existence: he offers a theory of the elasticity of the air, and founds many curious experiments on this property.

It is scarcely necessary to insist on the paramount importance of our atmosphere to us. Without it the earth would be as arid and as lifeless as the moon. We owe to it the numberless changes which constitute the phenomena of weather, and the gradual transition of day into night and of night into day; by its power of retaining and modifying the heat of the sun, it preserves unscorched the face of the earth; and by its property of conducting sound, it affords us the means of intercourse by speech. It effects the disintegration of rocks, and the creation of soils. It maintains the vitality of everything living, and achieves its destruction after death.

73. Its Extent.—On the authority of Wollaston, it was long considered that the atmosphere round our earth was limited in extent. From observations made on the duration of twilight, Wollaston concluded that the atmosphere extended to a height of about 45 miles. It is far more probable, however, that no such limit exists, but that the atmosphere extends through space. It has been shown by mathematical reasoning that it must extend even to the moon, but that its density there is scarcely appreciable by direct measurement, as it cannot exceed the 1-800th part of that of our atmosphere at the earth's surface: it has been calculated that the moon's atmosphere would support a column of mercury about one millimetre high.

It is evident, from a variety of causes, that the density of

the atmosphere round the earth cannot be the same at all points. From the increase of attraction at the poles, and from its diminution at the equator,—from the increase of temperature on approaching the torrid zone, and especially from the action of centrifugal force, which is greatest at the equator, and is *nil* at the poles,—the mass of the atmosphere round our planet would present to an exaggerated degree its form of an oblate spheroid, whose polar diameter is considerably shorter than its equatorial diameter.

74. Its Pressure.—The average weight of the atmosphere at the sea's level in our latitudes is equivalent to that of a column of mercury 760 millimetres high: this is equal to a pressure of 103·3 kilos upon a square decimeter, or 14·73 English pounds upon a square inch. To obtain the total weight of the atmosphere in kilograms, we have merely to multiply the number of square centimetres on the surface of the earth by 103·3. The weight thus obtained amounts to 5·3 billions of kilos.

In the same manner, we can readily calculate the weight of the atmosphere pressing upon the surface of our bodies: we shall find it to amount to several tons. The human frame is so constituted, that the absence, or even a considerable diminution, of this pressure would cause a serious if not a total disarrangement of our economy. It has been shown that certain bones, particularly the thigh bones, together with the ball and socket hip joint, are in certain positions only kept in place by the pressure of the atmosphere. The hæmorrhage occasionally experienced during balloon ascents is due to the bursting of the small blood-vessels situated in the region of the eyes, nose, and mouth, from the rapid and too forcible propulsion of the blood consequent on the decrease in atmospheric pressure. This hæmorrhage is more particularly confined to aeronauts, as travellers in ascending high mountains in general feel no such inconvenience, their gradual ascension affording time for them to become accustomed to the decreased pressure.

75. Variations in the height of the Barometer.—It was quickly observed after the invention of the barometer that its height or, what amounts to the same thing, the atmospheric pressure was subject to variation at the same locality. These

variations were first noticed by Descartes. The pressure of the atmosphere varies with the latitude of the place, the seasons of the year, and the hour of the day. At London, the mean height of the barometer is 759·0 m.m.; at Paris it is 760·0 m.m. The pressure increases generally as we approach the poles from the equator, attaining a maximum at 30° N. lat., after which it decreases to a minimum at 65°, when it again begins to rise. The maximum at 30° is attributed to the influence of the trade-winds at those regions. The mean height of the barometer is lowest in the tropics, especially under the equator; this is probably due to uprising air-currents. The following table shows the relation between the latitude and the height of the barometer :—

Lat.	H.	Lat.	H.	Lat.	H.	Lat.	H.
°	m.m.	°	m.m.	°	m.m.	°	m.m.
0	760·20	30	764·60	49	761·41	60	756·97
10	761·34	40	762·47	51½	760·73	64	751·97
20	763·61	45	762·00	54½	760·10	67	753·67

The pressure of the atmosphere varies also with the seasons of the year. It is found that two maxima occur, one in summer and the other in winter; the minima being in spring and autumn. The maximum in summer is at first sight contrary to what we should expect. Radiation from the earth's surface creates ascending currents and diminished pressure. We should therefore anticipate a low barometer at this season of the year, which indeed would actually occur, did not an increased evaporation of water more than compensate for the influence of the uprising currents. The yearly variations in the pressure of the atmosphere have only been determined for a few places, and it appears that there are well authenticated exceptions to the above law. Within a zone extending to the parallel of 40° on either side of the equator, the greatest and least atmosphere pressures appear to correspond with the greatest and least zenith distances of the sun. Thus, at Madras (lat. 13° 4' N.), the mean height of the barometer in January is 5·34 m.m. greater than in July.

At Calcutta (lat. $22^{\circ} 30' N.$), the difference amounts to 13.2 m.m. At the Cape of Good Hope (lat. $34^{\circ} S.$), the height is 7.36 m.m. greater in January than in July.

Apart from the accidental fluctuations of the barometer, due to the influence of storms and hurricanes, there is a regular horary oscillation which, in the tropics, presents two maxima—viz., at about 9 a.m. and 10.30 p.m., and two minima at 4 p.m. and 4 a.m. The regularity of this oscillation within the tropics is such that the hour of the day may be approximately ascertained from the height of the mercurial column. This fluctuation is not confined to the level of the sea, but takes place with equal regularity at altitudes of 13,000 feet. The amplitude of this oscillation is about 2.2 m.m. within the tropics. As we approach the poles the amount becomes less, until, at $70^{\circ} N.$ lat., it is only 0.3 m.m. In our latitudes these variations are in general masked by accidental causes, but by comparing the results of a large number of observations they can be clearly detected. In Paris, observations extending over eleven years show that the variation amounts to 0.756 m.m. from 9 A.M. to 3 P.M., and to 0.373 m.m. from 3 P.M. to 9 P.M. The amount appears to differ during the seasons of the year, being greater in summer than in winter.

It follows from the law of Boyle, that the air, being an elastic fluid, is composed of strata of different density. The stratum at the surface of the earth being subjected to the pressure of the superincumbent air, is denser than the one immediately above it. In proportion as we ascend, we find that each stratum becomes rarer than the one just below it. Hence the importance of the barometer as a measurer of heights. The fact that the mercurial column stands lower at the top of an elevation than at the bottom was first noticed by Claudio Bereguardi at Pisa, and five years later by Perrier, who, at the suggestion of Pascal, ascended the Puy de Dome in 1648 for the purpose of making the observation. Pascal did not fail to point out how strongly this observation corroborated the truth of Galileo's explanation of atmospheric pressure.

The following table shows the pressure and density of air at different altitudes:—

Metres above Sea-Level.	Bulk of Equal Weight of Air.	Density.	Barometer.
0	1 c. metre	1	m.m. 760
5,520	2 "	0.5	380
11,040	4 "	0.25	190
16,040	8 "	0.125	95
22,080	16 "	0.0625	47.5
27,600	32 "	0.0312	23.8

It has been calculated that, if the bulk of a given weight of air continued to vary at the above rates, one cubic inch of air measured at the earth's surface would, at the distance of 4,000 miles, fill a space as large as Saturn's orbit; on the other hand, at a distance of only 46 miles below the surface of the earth, the air would have the density of mercury.

76. Relations of the Atmosphere to Heat.—The atmosphere appears to receive its heat in the following ways—(1.) From the direct rays of the sun; (2.) From the reverberation of those rays from the earth's surface; (3.) By contact with the ground; (4.) From the action of aqueous vapour.

Air appears to be *diathermanous*—i. e., it does not absolutely act as a vacuum in the transmission of radiant heat. The heat received by the atmosphere from the direct rays of the sun must be considered, however, as the least important of the four principal sources just enumerated. The greater part of the heat which finds its way into the atmosphere is generally considered to be due to radiation from the earth's surface, and to the contact of the air with the ground. The amount of heat thus sent into the air will of course vary considerably even in places in the same latitude, and not very far distant from each other, since it mainly depends on the nature of the soil which receives the solar rays. This fact is important as an element in the classification of climates. It has been shown that places in the same latitude, not very far apart, and in the same condition as regards protection, may have very different mean temperatures on account of the different capacities of various soils for absorbing and retaining heat.

Aqueous vapour is undoubtedly one of the most important agents in augmenting the temperature of the atmosphere.

This must be evident, when we consider the enormous amount of heat which is rendered latent in the process of the evaporation of water from the earth's surface, and which again becomes sensible on the condensation of the vapour in the upper regions of the air. Aqueous vapour, however, appears to act as an agent in communicating heat to the air, even when in the condition of perfect gaseity, by retarding the transmission of heat rays through the air.

77. The Atmosphere in its Chemical Relations.—The chemical history of the atmosphere can, in strict truth, be said to date only from the early part of the 17th century. Up to that time the air was considered as akin in nature to fire. There was no decided opinion of its materiality, although it was held to enter into the composition of many bodies. It was considered to be essential to animals, as light was supposed to be necessary to plants.

Many metals, when exposed to fire, lose their brilliancy, and become covered with an opaque, lustreless, earthy substance, termed by the older chemists a *calx*. As this *calx* is formed, the metal increases in weight. This fact has been known from very early times. Geber, in the 8th century, speaks clearly on this point in the case of lead and tin. Cardan (1501–1576) even mentions that the gas (*flatus*), which increases the weight of the lead, exists in nitre, feeds flame, and rekindles a body presenting an ignited point. Rey, in France, first clearly proved that the formation of the *calx*, and the augmentation of the weight of the metal, entirely depended on the access of air; and Hooke and Mayow, in England, appear to have first traced the analogy between combustion and respiration. Both the later philosophers showed that the air contained a principle analogous to, if not identical with, that contained in nitre; and both proved, by experiment, that a portion only of the air is required for combustion and respiration. Boyle, in 1692, conclusively showed that air was absorbed during the calcination of metals, by heating lead and tin in hermetically sealed vessels, for lengthened periods, at a high temperature. When the vessels were again cold, he was able, on making small apertures in them, to perceive the sound of air rushing in to supply the partial vacuum.

The clear interpretation of these phenomena was reserved, however, for Lavoisier. It had long been known that mercury, when heated, becomes covered with a calx, and increases in weight. The fact was even recorded by Sulzbach, an alchemist, living in the 15th century. He further showed that the substance which increases the weight of the metal is again disengaged on heating the artificial cinnabar, as he terms the mercuric oxide. Lavoisier placed about 4 ounces of mercury in a matrass or flask of about 36 cubic inches in

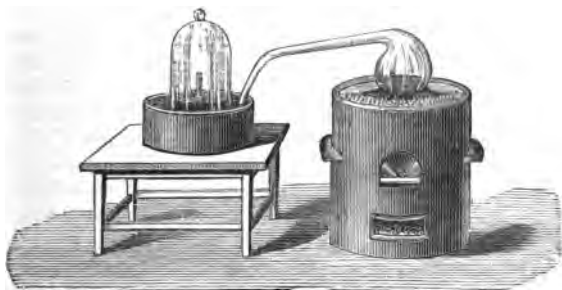


Fig. 60.

capacity, the neck of which was from 6 to 7 lines in diameter. It was drawn out and recurved in such a manner that the end appeared above the level of the mercury in a partially filled graduated glass jar placed in a mercurial trough (fig. 60).

The height of the mercury in the graduated jar was carefully noted, together with the temperature of the enclosed air, and the metal in the flask was gradually heated to within a few degrees of its boiling point, and maintained at this point during twelve successive days. During the first day no remarkable phenomena were manifested; the evaporated mercury condensed in little drops on the higher and cooler parts of the flask. On the second day, small red particles were observed on the surface of the heated mercury, and these increased in number during four or five days. On the termination of the experiment, it was found that the air contained in the graduated jar had diminished in volume, and that, instead of the 50 cubic inches originally taken,

there remained only 42 or 43 cubic inches. The gas in the graduated jar no longer supported combustion. The calx of mercury (mercuric oxide) was collected; its weight amounted to 45 grains. Heated in a small retort, it was entirely resolved into mercury and oxygen; the volume of the evolved gas was about 8 cubic inches. By mixing the two gases thus isolated, Lavoisier reconstituted atmospheric air equal in volume to that originally taken.

78. Composition of the Air.—It was thus clearly established that air was composed of oxygen—the empyreal air of Priestley and Scheele; and of nitrogen—the gas discovered by Rutherford. Many methods were now devised to measure the amount of the oxygen, since it was assumed that the comparative wholesomeness of the air depended on the proportion of its oxygen. Hence originated the art of eudiometry (from *eûdios*, good, serene; and *μέτρον*, a measure); that is, the art of measuring the goodness of air. Careful experimenters, however, were not able to find the differences in the composition of good and bad air which their theories demanded; air which was reputed to be unhealthy could not be distinguished from that which experience had found to be beneficial and salubrious. Cavendish made upwards of 500 analyses of town and country air, in winter and summer, and in wet and clear weather, without detecting any appreciable differences. As the mean of all his trials, he found that 100 volumes of air contained—*

Oxygen,	20.833
Nitrogen,	79.167
	<hr/>
	100.000

Cavendish clearly pointed out the nature and extent of the information supplied by the eudiometer; etymologically, the name had no longer any significance. "In so far," he says, "as the instrument takes cognizance of the impurity of the atmosphere, it betrays no difference between one specimen of air and another; so that, apparently, there are no degrees of goodness to be measured. . . . Thus it may be inferred that our sense of smelling can, in many cases, perceive infi-

* Calculated by Wilson. (See *Life of Cavendish*, p. 229).

nately smaller alterations in the purity of the air than can be perceived by the nitrous test"—i. e., by the eudiometric method which he employed. (*Vide infra*).

79. Air a Mechanical Mixture.—The constant proportion of the two principal constituents of the atmosphere appeared now to be so well established that many chemists inclined to the opinion that air was a chemical compound of oxygen and nitrogen. Many reasons, however, conduce to show that the air is simply a mechanical mixture of its constituent gases. In the first place, the relative amounts of the two gases are not those of their combining weights, nor of any simple multiple of those weights. We can obtain atmospheric air by mixing oxygen and nitrogen in the proportion of 20·9 vols. of the former to 79·1 of the latter; none of the ordinary manifestations of chemical action—such as the development of heat or of electricity or change of volume—occurs when the gases are thus mixed. In the second place, we find that air is dissolved by water to a slight extent; on boiling the water, the air is again expelled. If air were a chemical compound, it ought to possess the same composition before and after solution. Experiment shows, however, that the air expelled from water by boiling invariably contains more oxygen than ordinary air, in consequence of the greater solubility of that gas as compared with nitrogen—

	Before Solution.	After Solution.
Oxygen,.....	20·96	35·91
Nitrogen,.....	79·04	65·09
	<hr/> 100·0	<hr/> 100·0

In the third place, it is found that the refractive power of air is equal to the mean of the refractive powers of its constituents; whereas, in compound gases, the refractive power is always either greater or less than the mean refractive power of their elements.

80. Subject to very slight Changes in Composition.—Although the composition of the atmosphere is marvellously constant, when we consider the numberless agencies at work which tend to modify the relative proportion of oxygen and nitrogen, still the refined experiments of Bunsen and Regnault have shown that the air is in reality subject to

slight, although perfectly appreciable, variations in composition. The former chemist found the extreme differences in the proportion of oxygen, in fifteen analyses of air collected at different times in the same locality, to be 20·970 – 20·840 per cent.; the latter found, in upwards of one hundred analyses of the air of Paris, differences of 20·999 and 20·913; country air showed differences of 20·903 and 21·000; air collected over the sea, in various parts of the world, showed extremes of 20·940 and 20·850.*

The composition of the air by weight was determined by Dumas and Boussingault. Air, carefully freed from water and carbon dioxide, was aspirated over ignited metallic copper: the heated metal combined with the oxygen to form cupric oxide, and the nitrogen passed into an exhausted balloon. The increase in the weight of the metal gave the amount of oxygen, and the increase in the weight of the balloon that of the nitrogen, in the air. As the mean of a number of experiments made by this method, Dumas and Boussingault found that 100 parts by weight of air contained—

Oxygen,	23·00
Nitrogen,	77·00
	100·00

We have comparatively little information with regard to the relative proportion of the constituents of the air at great elevations. Up to a height of 3,000 metres, air appears to have sensibly the same composition as at the earth's surface.

* Several very marked deviations were occasionally observed by Regnault:—1. Air collected from the port of Algiers, about 11 p.m., June 5, 1851, gave (1.) 20·420, and (2.) 20·395 per cent. of oxygen. 2. Air collected in the Gulf of Bengal, lat. 9° 4', long. 83° (Paris), at mid-day, February 1, 1849, gave 20·460 and 20·453 per cent. of oxygen. 3. Air from mouth of Ganges, near Calcutta, collected at noon, March 8, 1849, weather foggy, breeze N.E., gave 20·390 and 20·387 per cent. of oxygen. The banks of the river were covered with animal and vegetable debris during the recession of the tide, and cholera was raging in the district. It is possible, however, that this diminution might have been effected by the subsequent action of organic matter drawn into the tube in the aspiration of the air. The amount of carbonic acid in the sample (which was simultaneously determined) was excessive, viz., 0·33 per cent.; a portion of this was probably formed by the oxidation of the organic matter in the tube.

Among the agencies tending to abstract the oxygen from the air may be enumerated—(1.) The respiration of animals; (2.) The combustion of organic matter; (3.) The decay and putrefaction of organic substances; (4.) The disintegration of rocks; and (5.) The ultimate oxidation of inorganic matter, *e. g.*, in the conversion of the protoxides of iron and manganese, &c., to the state of peroxides. In the last case, oxygen would appear to be permanently lost to the atmosphere, for it is only in rare instances that it can be again restored by processes of reduction. A very little calculation, however, serves to show that the reservoir of oxygen contained in the atmosphere amply suffices to maintain its numerous functions. If we suppose the atmosphere to be put into a balloon, and suspended from the end of a balance, it would require 581,000 cubes of copper, each having a side of 1 kilometre in length, to restore equilibrium. If we also assume that each individual consumes 1 kilo. of oxygen *per diem*, and that the population of the earth is one thousand millions, and, further, that the oxygen consumed in the respiration of other animals, and in the oxidation of organic matter, amounts to four times that required by man, and also that the oxygen disengaged by plants compensates only for the causes of diminution of oxygen not specified,—then, even in this exaggerated case, the amount of oxygen abstracted from the air in a century would only amount to fifteen or sixteen of the copper cubes; or, in other words, the abstraction in a century would be only $\frac{1}{80000}$ th of the total quantity of oxygen contained in the air—an amount inappreciable by the most exact eudiometric methods known to us.

81. Ozone.—It has been clearly demonstrated that ozone exists in the air, but at present we know very little of the circumstances which influence its production. From the observations of Houzeau, it appears that country air contains about 1 part of ozone in 450,000 parts of air by weight, or 1 volume in 700,000 volumes of air. It has been stated that there is an intimate relation between the quantity of ozone in the air and the development of atmospheric electricity. The frequency of ozone manifestations varies with the seasons, being greatest in spring, strong in summer, weaker in autumn, and still weaker in winter. Other observations, however,

seem to show that the amount of ozone in air unexposed to the influence of the land is very nearly constant.

It is remarkable that the air over marshes, or in places infested by malaria, contains little or no ozone; but that, as we ascend heights above such localities, the amount of ozone rapidly increases. No ozone can be detected in large cities, or in the air of dwelling rooms. There can be little doubt respecting the function of ozone in the atmosphere: one at least of its uses is to oxidize and render innocuous the putrescent organic matter which is being continually sent into the air. It is highly probable that the salubrity of country air, and the depressing effect of the air of towns, is intimately related to the presence or absence of ozone, and to its action on organic matter.

82. Aqueous Vapour in Air.—Aqueous vapour is always

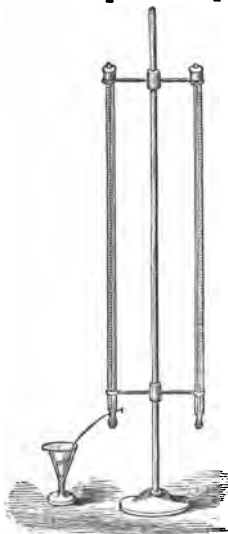


Fig. 61.

present in the air, although in very variable quantity. The humidity of the air depends principally upon its temperature, upon the direction and succession of winds, on the distance from the equator and the sea's level, and on the manner in which the moisture is precipitated. The most accurate method of determining the amount of aqueous vapour in the atmosphere is to aspirate a known volume of air through a series of weighed tubes filled with calcium chloride, or some other hygroscopic substance. The increase in the weight of the tubes gives the amount of aqueous vapour present in the volume of air. This method is, however, tedious, and inapplicable to the determination of the moisture contained in the air at any given moment. Accordingly, meteorologists have recourse to *hygrometers*. One of the simplest and most reliable of these instruments is represented in fig. 61. It consists of two precisely similar thermometers placed side by side. The bulb of one thermometer is covered with muslin, kept constantly moistened by the capillary action of an attached piece of thread

or lamp wick dipping into a cistern of water. The evaporation of water from the muslin lowers the temperature of the thermometer, and the rapidity of the evaporation (and consequently the degree of cold) is proportional to the dryness of the air. Tables have been constructed showing the humidity of the air from its temperature, and from the difference in the two thermometer readings.

The air rarely contains the amount of aqueous vapour necessary to saturate it. In some parts of Central Asia, Russia, Africa, and in the neighbourhood of the Red Sea, extraordinary degrees of dryness have been noticed; but in our more humid climate saturation is sometimes very nearly attained.

83. Carbon Dioxide is an invariable constituent of air: its presence in the atmosphere was demonstrated by Macbride in 1764, from the observation that quicklime, after long exposure to the air, acquired the property of effervescing with acids. The first exact determinations of its amount were made by Thenard in 1812. His process consisted in exhausting a large glass balloon, of about 10 litres capacity, in which baryta water was previously placed. By turning the stopcock a fresh quantity of air was allowed to enter the globe: this was permitted to remain in contact with the baryta water for some time, the absorption of the carbon dioxide being promoted by shaking the balloon. The process of exhaustion and replenishment was repeated until a sufficient quantity of barium carbonate was formed. From its weight, together with the number of times of exhaustion, the amount of the carbon dioxide in the air could be calculated. Thenard found that the proportion of this gas was about 4 volumes in 10,000 volumes of air.

The subsequent researches of Saussure, Boussingault, Angus Smith, and Roscoe have confirmed this result. They have further shown that the amount of carbon dioxide in air is not absolutely constant. It would appear that during the night the amount of carbon dioxide increases: it is sensibly greater during the prevalence of dry winds and during fogs, as much as 8 or 9 volumes of carbon dioxide in 10,000 volumes of air being frequently noticed on a foggy day. Country air also contains less carbon dioxide than the air of large towns. Sea air contains less carbon dioxide than land air. As the

mean of a number of observations made on the air of the Irish Sea and of the Atlantic Ocean, it appears that 10,000 vols. of sea air contains 3 vols. of carbon dioxide. This proportion is constant in various latitudes, and is not affected by the differences in the season of the year or hour of the day.

According to Saussure, air in the upper parts of the atmosphere contains more carbon dioxide than air at the surface of the earth.

A very important relation, first pointed out by Priestley and Ingenhousz, exists between the carbon dioxide and oxygen in the air. By the combustion of organic matter and the oxidation of the waste tissue of animals, carbon dioxide is continuously sent into the atmosphere. Unless, therefore, some compensating influence were at work, the air would experience a gradual diminution in the proportion of oxygen, and an equally gradual increase in the amount of carbon dioxide. Such a compensating influence exists in the power possessed by plants of decomposing carbon dioxide. By the agency of the green portions of their structure they are able, under the influence of sunlight, to split up this gas, retaining the carbon and restoring the oxygen to the air. There is thus a continual circulation of oxygen and carbon between the animal and the plant. The oxygen serves as a carrier of one of the waste products of the animal to the plant; the plant in its turn decomposes this waste product, returns the vital oxygen to the atmosphere, and assimilates the carbon to form fresh food for the animal.

It has been observed that a square metre of leaf will decompose in sunlight more than a litre of carbon dioxide in an hour.

The atmosphere receives a large portion of its carbon dioxide from subterranean sources. The amount thus sent into the atmosphere is much greater than that produced by the respiration of animals, or by the combustion of organic matter. Poggendorff has calculated that the amount of the carbon dioxide which thus finds its way into the air is at least ten times greater than that produced from all other sources in conjunction; and that if no causes of diminution existed, the amount of carbon dioxide in the air would be doubled in about 380 years.

84. Nitric Acid, or some lower oxide of nitrogen, is a very frequent, if not an invariable, constituent of air. Its presence

in the atmosphere was first observed by Priestley. Its formation is in great part due to electrical discharges in the air; the first portions of the rain collected in the country during severe thunder-storms have invariably an acid reaction from the presence of dissolved nitric acid. In tropical regions such electrical discharges are of very frequent occurrence, and possibly a large portion of the nitric acid existing on the earth in these regions, as potassium and sodium nitrates, has its origin in this combination of atmospheric oxygen and nitrogen. Nitric acid is in all probability likewise formed by the action of ozone upon atmospheric ammonia. One million parts of rain water collected in the country contain on the average about 0.5 part of nitric acid. The amount increases in the rain water of towns. As the average of a number of determinations made in English towns, Dr. R. Angus Smith found 0.86 parts per million. In densely populated districts the amount often considerably exceeds this quantity: thus, in Glasgow the average of a number of determinations gave 2.436 parts in a million.*

85. **Ammonia** is also present in the atmosphere. Scheele observed long ago that a bottle containing hydrochloric acid became coated with ammonium chloride on exposure to the air. A piece of clay heated to redness, and exposed to the air for a few days, yields a perceptible amount of ammonia when re-heated: this is not the case if the clay be kept in a stoppered bottle. Aluminium sulphate in like manner is ultimately converted into ammonia alum by prolonged exposure to the air.

The amount of the ammonia contained in the air has been variously estimated: the results on record vary from 135 to 0.1 of ammonia (calculated as carbonate) in 1,000,000 parts of air. Fresenius found that 1,000,000 parts by weight of air contained during the day 0.098 parts of ammonia, and during the night 0.169 parts. Recent observations by Mr. Horace T. Brown appear to show that the amount ordinarily contained in the air is much larger than this. It was found that a million parts of country air, when at a height of two metres from the ground, contained from 5.102 to 6.085 parts, and

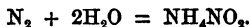
* R. Angus Smith, *Air and Rain*, p. 287.

the same amount of the air of a town contained from 4.059 to 8.732 parts of ammonium carbonate. Direction of the wind appears to have no influence on the amount of ammonia. The quantity apparently decreases after heavy rain, but it is restored to the normal amount (about 6 parts in 1,000,000 of air) in a few hours. (*Proc. Roy. Soc.*, March, 1870).

The proportion of ammonia contained in rain water is as variable as that contained in the air. It depends upon the condition of the atmosphere, and on the duration of previous drought. The first portions of rain-water contain more ammonia than the last. Messrs. Lawes and Gilbert found that 1,000,000 parts of rain water collected in the country contain from 0.927 to 1.142 parts of ammonia. Water collected in towns invariably contains a larger amount of ammonia than that collected in the country. Thus, Barral found that 1,000,000 parts of Paris rain water contained 3.49 parts of ammonia. Similar results have been obtained by Dr. Angus Smith. The rain water of inland country places in England contains, on the average, 1.07 parts of ammonia, exactly agreeing with the observations of Messrs. Lawes and Gilbert. The water collected in the inland country places and more sparsely populated districts in Scotland contained only 0.53 parts of ammonia per million. The rain water of London contained 3.45 parts; that of Liverpool, 5.38 parts; that of Manchester, 6.47 parts; and that of Glasgow, 9.10 parts per million. These numbers are in each case the mean of many observations. (*Loc. cit.*) The larger proportion in the cities is due to the influence of animal life, and to the constant presence of azotized organic matter in the air of thickly-populated districts. Ammonia is contained in the water of dews and fogs in larger quantity than in rain.

Small as these amounts of ammonia and nitric acid may appear, they yet play a very important rôle in vegetation; they constitute the source from which plants obtain the nitrogen needed for the formation of their seed and other parts of their structure. Plants appear not to possess the power of directly assimilating the free nitrogen from the air; if placed in an atmosphere and in a soil free from ammonia and nitric acid, and from substances which can generate these compounds, they gradually languish, and ultimately die.

It was noticed by Schönbein that ammonium nitrite is produced by the evaporation of pure water in the air. If a piece of clean linen or calico, drenched with distilled water and dried in the open air, be again moistened with pure water, the liquid which drops from the fabric, after being acidulated with pure sulphuric acid, will give the reactions of nitrous acid; for example, it will render iodized starch-paper blue. Similarly, if pure water be heated to 50° or 60° , and filter-paper, moistened with a solution of pure sodium carbonate, be suspended in the steam, in a very short time (10 or 15 minutes) the paper will give the reactions of nitrous acid—



Since water is constantly evaporating from its surface (and of course from the ground in its vicinity), it is probable that the plant may thus obtain, and indeed prepare for itself, a portion of its nitrogenous food.

So far as we at present know, the only essential and necessary constituents of atmospheric air are oxygen, nitrogen, carbon dioxide, aqueous vapour, ozone, ammonia, and nitric or nitrous acids. Ten thousand volumes of pure atmospheric air may be represented to contain:—

Oxygen,.....	2065.94
Nitrogen,.....	7790.60
Carbon dioxide,	3.36
Ozone,.....	0.015
Aqueous vapour,	140.00
Ammonia,.....	0.08
Nitric acid,	0.005
	<hr/>
	10,000.000

86. Accidental Impurities in Air.—Rain water, collected in vessels upon which it exerts no solvent action, is invariably found to contain saline substances and organic matter, derived from the atmosphere. Moreover, we find that the moisture condensed from air contains organic matter, dead and living. Moscati, more than sixty years ago, observed that the hoar-frost, condensed on bottles filled with ice, and suspended over the rice-fields of Tuscany, yielded a perfectly transparent liquid on thawing; this, in a short time, deposited flakes of a body containing nitrogen, and

quickly became putrid. The same appearances were noticed by Regaud de Lisle in the dew of the marshes of Languedoc. Vogel further observed that the moisture condensed on cold surfaces, placed in the air of an apartment containing many persons, quickly became putrid, owing to the presence of animal matter resembling impure albumen.

Dr. Angus Smith has more minutely investigated the nature of the substance condensed from the breath. If allowed to stand for some time, it forms a thick, glutinous mass, which, when examined by a microscope, is seen to be a closely-matted, confervoid growth. Between the stalks of the confervæ are to be seen a number of greenish globules constantly moving about, various species of volvox, accompanied also by monads many times smaller.

The nature of the substances present in rain has also been investigated by Dr. R. Angus Smith, who has shown that the examination of rain water affords a method of determining the impurities in air, and hence, probably, its comparative sanitary value. As the results of a large number of experiments, he finds that rain falling through the air over the sea contains chiefly common salt; it also contains sulphates, and in larger proportion to the chlorides than is found in sea-water. The sulphates increase inland, before large towns are reached. They seem to be a measure of the products of decomposition, the sulphuretted hydrogen evolved in the putrefaction of organic compounds being oxidized in the atmosphere. In large towns, the amount of the sulphates is greatly increased, owing to the combustion of coal, which contains iron pyrites (FeS_2), as well as to the larger amount of sulphuretted compounds derived from the putrefaction or decomposition of organic matter. The rain water of large towns is not unfrequently acid, owing to the presence of free sulphuric acid; free acids are not found with certainty in rain water removed from the influence of combustion or manufactures. When the rain contains 40 parts per million of free acids, the vegetation of the district is rapidly affected. Ammoniacal salts increase in the rain in the neighbourhood of towns. They come partly from coal, and partly from the decomposition of albuminoid substances. The following analyses by Dr. Smith will show the

general character of the rain water (and therefore of the impurity of the atmosphere) in various parts of Great Britain.* The results are the mean of many experiments; they are expressed in parts per million:—

	I.	II.	III.	IV.	V.	VI.	VII.
Sea air—Scotland,.....	12.28	3.61	0	0.74	.105	.424	.018
England,.....	—	5.88	0	1.90	—	.871	—
Inland county air—Scotland,...	3.37	2.06	0	0.53	.04	.305	.264
England,...	3.99	5.22	0	1.07	.109	.749	.460
Towns—London,.....	1.25	20.49	3.87	3.45	.205	.840	—
Liverpool,.....	10.16	39.59	11.56	5.38	.159	.582	3.896
Manchester,.....	5.83	44.82	10.17	6.47	.251	1.032	4.401
Glasgow,.....	8.97	70.19	15.13	9.10	.300	2.436	10.040

- I. Amount of hydrochloric acid (chlorides).
 II. " sulphuric acid (sulphates).
 III. " acidity (free sulphuric acid).
 IV. " ammonia.
 V. " albuminoid ammonia (decomposition of organic matter).
 VI. " nitric acid.
 VII. " weight of oxygen required to oxidize organic matter (measure of organic matter and nitrates).

CHAPTER VIII.

COMPOUNDS OF NITROGEN WITH HYDROGEN AND OXYGEN.

87. Ammonia.— NH_3 . Mol. weight 17. Density 8.5.

This gas, the only known compound of nitrogen and hydrogen, was discovered by Priestley in 1774. It may be formed by the direct union of its elements in the free state, but it is more readily produced by their combination in the *nascent* condition—i. e., in the moment of their liberation from other compounds. Water containing atmospheric air in solution yields ammonia at the negative pole during its electrolytic decomposition. We have already stated that ammonium nitrite is formed during the evaporation of water in the air. When a mixture of barium monoxide and carbonaceous matter is heated in air barium cyanide is pro-

* R. A. Smith, *Air and Rain*. London: 1872.

duced; this compound is decomposed by steam at 300° , forming barium carbonate and ammonia. This process has been proposed as a method of obtaining ammonia on the large scale from the nitrogen of the air. Azotized organic matter yields ammonia during putrefaction or by distillation: probably the main portion of the naturally existing ammonia has been derived from putrefactive changes.

The ammonia of commerce is in great part produced by the destructive distillation of coal. This substance is composed of carbon, hydrogen, oxygen, and nitrogen. When heated in closed vessels, as in the manufacture of coal gas, the greater portion of the nitrogen unites with hydrogen to form ammonia, which condenses in the water simultaneously liberated. The ammoniacal liquor of the gas-works is neutralized with sulphuric or hydrochloric acid, the solution is evaporated to dryness, and the resulting saline mass purified by sublimation or re-crystallization. Or a current of steam is blown through the liquor, whereby the ammonia is expelled in the gaseous form, and is received in diluted oil of vitriol, when ammonium sulphate separates out.

88. Preparation and Properties of Ammonia.—When the compounds of ammonia are heated with caustic potash or soda, or with the alkaline earths, they are decomposed with the evolution of the ammonia. In the case of sal-ammoniac and lime the reaction may be thus represented—



Ammonium chloride and lime give ammonia, water, and calcium chloride. In practice it is advisable to use a larger proportion of lime than is demanded by the above equation, in order to insure the complete decomposition of the ammoniacal salt. The ammonia is disengaged, even in the cold, and very rapidly on the application of a gentle heat.

Ammonia is $\frac{17.0}{16.0} = 1.0625$ times lighter than air. Accordingly, it may be collected by *upward displacement*. Fig. 62 represents the apparatus which serves for the preparation and collection of ammonia. The flask *a* contains the mixture of lime and sal-ammoniac; the cylinder *b* is filled with lumps of quicklime, which serve to dry the gas. Ammonia may be collected over mercury, but not over water, by reason of its great solubility in that liquid. One gram of water at 0°

absorbs 0.877 gram, or 1.149 times its volume of ammonia gas under the ordinary pressure of the atmosphere. It has

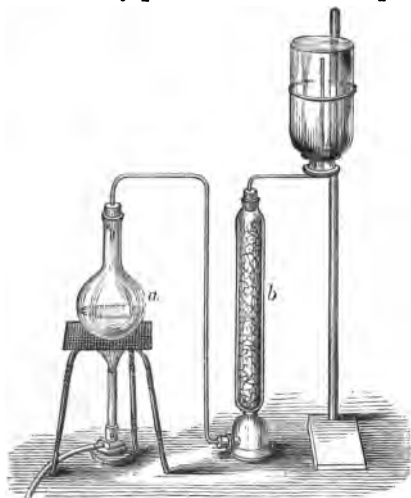


Fig. 62.

already been stated that the solubility of the gas rapidly diminishes with the increase of temperature. Thus, at 20° , 1 gram of water absorbs only 0.52 gram, or 681 times its volume of the gas under a pressure of 760 m.m. When heated to 100° water gives up its dissolved ammonia. In the act of absorption the solvent increases considerably in bulk: the strongest solution of ammonia has a specific gravity of 0.88. It freezes at -38° , forming a gelatinous mass, possessing very little odour. The ready solubility of ammonia in water may be demonstrated by placing a vessel filled with the gas over the liquid; the water will be forcibly driven into the vessel, owing to the rapidity of the absorption. (Fig. 63.)

Solution of ammonia has the power of dissolving many salts and oxides which are insoluble in water—*e. g.*, the oxides of copper, silver, zinc, &c., the chloride and phosphate of silver, &c.

Pure ammonia gas has a pungent odour, and a strong

alkaline reaction (whence the name *alkaline air* originally given to it by Priestley): it turns reddened litmus paper blue,

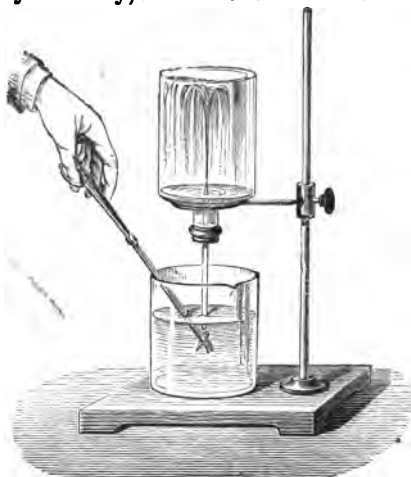


Fig. 63.

and renders yellow turmeric paper brown. These colours disappear after a time when the papers are exposed to the air, owing to the dissipation of the ammonia. Ammonia is a non-supporter of combustion and of respiration: animals die when immersed in the gas. It is feebly combustible: if a stream of oxygen be mixed with ammonia, evolved from a strong aqueous solution in the manner represented in fig. 64, the ammonia will burn with a greenish-yellow flame, if ignited at the end of the tube.

Ammonia may be condensed to a liquid by cooling it to -40° by means of a mixture of calcium chloride and snow. It may more readily be obtained in the liquid condition by taking advantage of the property possessed by certain metallic chlorides of absorbing large quantities of ammonia, and of again liberating the gas at a gentle heat. One-half of a strong glass tube is partially filled with dry silver chloride, and the tube is bent in the shape of the letter V; the chloride is then saturated with dry ammonia (it takes up about $\frac{1}{10}$ of

its weight of the gas), and the tube is carefully sealed. The empty limb is then placed in a freezing mixture, and the

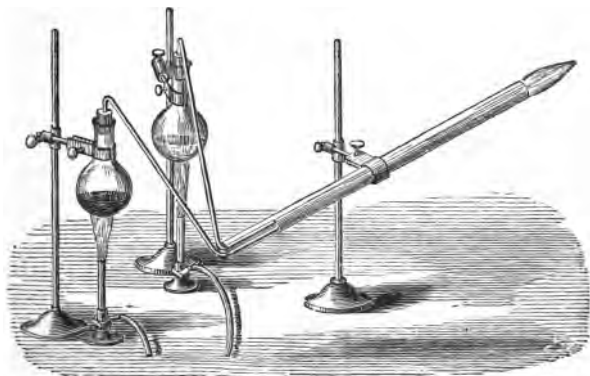


Fig. 64.

other limb, containing the ammoniated silver chloride, is gently heated. The chloride fuses at 38° , and at about 115° gives off its ammonia, which condenses in the cooled limb, by its own pressure, to a clear, mobile, highly refracting liquid, of sp. gr. 0.6234, at 0° . On removing the lamp, the silver chloride re-absorbs the liquefied ammonia with such rapidity that the liquid boils. The temperature of the boiling liquid is about -36° . Its vapour-tension at -30° is 866 m.m.; at 0° , 3,183 m.m.; at $+10^{\circ}$, 4,574 m.m.; and at $+20^{\circ}$, 6,388 m.m.—*i. e.*, it requires a pressure of 6 atmospheres to liquefy ammonia at 10° , and nearly 8.5 atmospheres at 20° .* Hence the advisability, in the process of liquefaction, of placing the empty limb of the V tube in a freezing mixture. Liquefied ammonia readily dissolves sulphur, phosphorus, iodine, and many salts. It dissolves the alkaline metals without change, forming azure-blue solutions. It is very expansible by heat; 1 vol. of the liquid, at 0° , becoming

* For a method of liquefying ammonia by expulsion from an alcoholic solution, see Müller, *Ann. d. Chem. u. Pharm.*, 157, 348. (1871.)

1.0215 vols. at 10°, and 1.045 vols. at 20°. By cooling to - 75°, it freezes to a transparent, ice-like mass, of greater specific gravity than the liquid.

If the limb of the tube containing the liquefied ammonia be placed in a wide test-tube, filled with water as the re-absorption of the gas by the

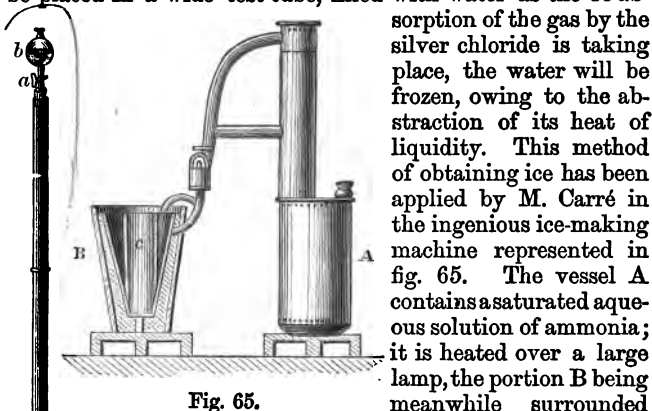
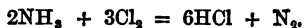


Fig. 65.

by cold water. At the increased temperature, the ammonia is expelled from its solution, and condenses, by its own pressure, in B. The lamp is removed, and A is now surrounded with cold water, when re-absorption commences; the liquid ammonia in B commences to boil, and robs the water contained in the inner vessel (c) of so much heat that it congeals.

89. Composition of Ammonia.—The fact that 2 vols. of ammonia are composed of 1 vol. of nitrogen, united to 3 vols. of hydrogen, was first determined by Fig. 66. Berthollet. The decomposition of the gas may be effected by means of the apparatus represented in fig. 66. The process depends upon the reaction which we have already employed for the preparation of nitrogen, viz., that when chlorine reacts upon ammonia, hydrochloric acid is formed, and nitrogen is eliminated—



A glass tube, about 1 metre long, is sealed at one end, and

divided into three equal parts (the divisions being conveniently marked by slipping caoutchouc bands over the tube). It is then filled with chlorine over the trough in the usual manner, and connected (under the trough) with the little stoppered globe *b*, containing strong aqueous ammonia. This is provided with a stopcock, *a*, in the tube, which passes through a perforated cork, by which it can be fixed into the tube in the manner seen in fig. 66. A drop of the ammonia solution is now allowed to fall into the atmosphere of chlorine. A lambent, yellowish-green flame marks the reaction between the chlorine and the ammonia. The ammoniacal solution is now brought, drop by drop, into the tube, when a dense white cloud of ammonium chloride is formed, which condenses upon the sides of the tube. When a column of 3 or 4 centimetres of ammonia solution has been introduced, the whole of the chlorine will have been converted into ammonium chloride by the combination of the hydrochloric acid with the excess of ammonia. By shaking the solution in the tube, the undissolved ammonium chloride may readily be removed from the glass. The disappearance of the chlorine is rendered evident by the loss of colour in the confined gas; it is no longer yellowish-green. The gas now in the tube is nitrogen. Its volume may be measured by fixing a little syphon to the mouth of the bulb, the longer limb of which dips into a dilute solution of hydrochloric acid, to neutralize the excess of ammonia. On gently turning the stopcock, the acid solution passes over into the tube. It continues to be driven over by atmospheric pressure, until the level of the liquid is coincident with the upper caoutchouc band. On removing the cork, a lighted taper plunged into the gas will immediately be extinguished. It is evident, therefore, that the volume of the nitrogen obtained is exactly one-third of the volume of chlorine taken. But since, as the equation tells us, chlorine unites with its own bulk of hydrogen, it is also evident that the nitrogen and hydrogen contained in ammonia are present in the proportion of 1 vol. of nitrogen to 3 vols. of hydrogen.

Ammonia is readily decomposed into its elements by passing it through a red-hot tube. It may also be decomposed by the electric spark. The sealed limb of the U tube (fig.

67) is filled to about one-third of its height with dry ammonia, and the volume of the gas is accurately measured by



Fig. 67.

bringing the levels of the mercury in the two limbs into coincidence. A series of electric sparks is then passed into the gas by means of the platinum wires melted into the tube. The volume of the confined gas immediately increases, and in about ten or fifteen minutes it will be seen (so soon as the levels of the mercury are again adjusted) to have become doubled. By allowing a little of the gas to escape through the stopcock, the pungent odour of the ammonia will no longer be perceptible, and, on the approach of a lighted taper, the hydrogen will inflame. These experiments teach us that, if we could effect its synthesis, we should find that 2 vols. of ammonia would be produced by the union of 1 vol. of nitrogen with 3 vols. of hydrogen.

90. Compounds of Nitrogen and Oxygen.—If hydrogen be caused to burn in a mixture of air and oxygen contained in a glass globe, red fumes are seen to be produced, and the condensed water is found to contain a considerable

quantity of nitric acid. It has already been mentioned that when a series of electric sparks is passed through air, the nitrogen combines with the oxygen. The production of the oxides of nitrogen is effected on the large scale in nature through the agency of atmospheric electricity. The combination of the two elements may be rendered

evident by means of the apparatus represented in fig. 68. The globe is filled with atmospheric air, through which a

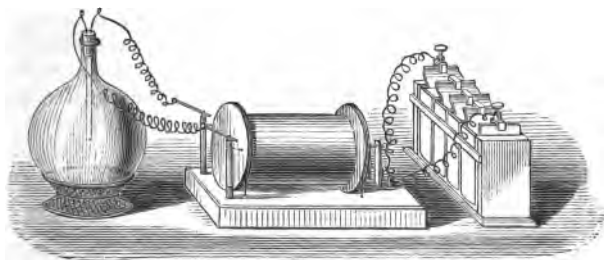


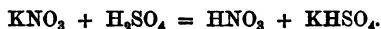
Fig. 68.

stream of electric sparks can be passed by the two wires. In a short time the globe becomes filled with ruddy fumes possessing an acid smell. These consist of the oxides of nitrogen. In presence of aqueous vapour, oxygen, and ozone, these red fumes become eventually converted into nitric acid, HNO_3 . The oxides of nitrogen have the power (like ozone) of liberating iodine from potassium iodide. If a moistened slip of iodized starch-paper be brought within the atmosphere in the globe, after the transmission of the sparks, it will be quickly turned blue.

All these agents, oxygen, nitrogen, aqueous vapour, and atmospheric electricity, exist in nature. Accordingly, in many parts of the world, as, for example, in India and Peru, we find depositions of nitrates formed by the action of atmospheric nitric acid upon the alkaline substances contained in the soil. From these nitrates we can again obtain the nitric acid, and by indirect means the remainder of the oxides of nitrogen.

91. Nitric Acid.—Symbol HNO_3 . Molecular weight 63.

When potassium nitrate is heated with sulphuric acid, nitric acid and potassium hydrogen sulphate are formed—



The apparatus represented in fig. 69 serves for the preparation of this acid on the small scale. The nitre is placed in

the retort and mixed with the amount of sulphuric acid demanded by the above equation. The nitric acid readily

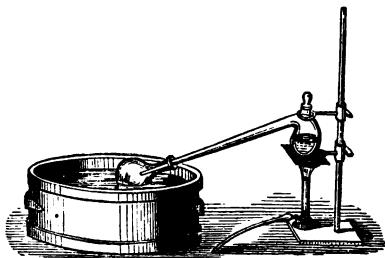


Fig. 69.

molecules of the nitrate are taken to one molecule of sulphuric acid—the sodium hydrogen sulphate being made to react

distils over at a gentle heat, and is collected in the cooled receiver. On the large scale sodium nitrate or Chili salt-petre is substituted for nitre, and the operation is conducted in large iron retorts connected with earthenware condensers, in the manner seen in fig. 70. Two

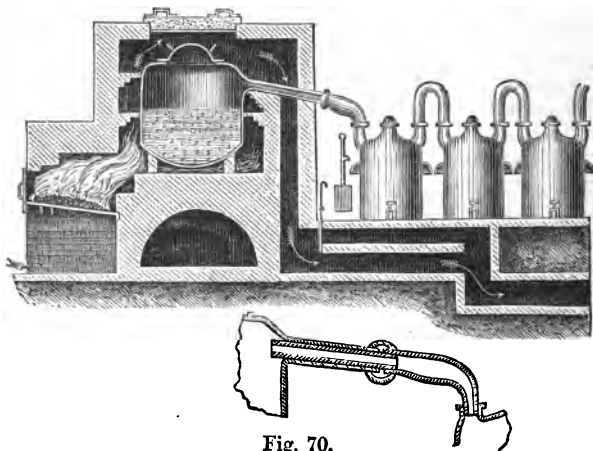
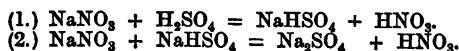


Fig. 70.

upon the second molecule of nitrate in accordance with the following reactions :—



A precisely similar reaction can be effected with potassium

nitrate, but sodium nitrate is preferred on the manufacturing scale for the reason that it is cheaper, and that a given weight of it can be made to yield a larger quantity of nitric acid than can be obtained from the same weight of nitre—

$$\begin{array}{rcccl} \text{KNO}_3 & = & \text{HNO}_3 & & \text{NaNO}_3 & = & \text{HNO}_3 \\ 39.1 + 14 + 48 & = & 1 + 14 + 48 & & 23 + 14 + 48 & = & 1 + 14 + 48 \\ \hline 101.1 & & 63 & & 85 & & 63. \end{array}$$

85 parts of sodium nitrate yielding the same amount of nitric acid as 101.1 parts of potassium nitrate.

Pure nitric acid is a colourless, strongly fuming liquid, of sp. gr. 1.559 at 0°, and 1.530 at 15°. The ordinary acid has generally a yellow colour, due to the presence of lower oxides of nitrogen, from which it may be freed by a current of air. When cooled to - 55° it freezes to a buttery mass. On heating, it gradually undergoes decomposition, and possesses no constant boiling point. If the strong acid be distilled, it appears to boil at 86°, and lower oxides of nitrogen are produced, and a residue is ultimately obtained containing 68 per cent. of HNO₃, and possessing a sp. gr. of 1.414 at 15°. If a weak acid be boiled under the ordinary pressure of the atmosphere, it gradually becomes concentrated until the above proportion of acid to water is obtained, when the acid distils over unchanged. The above relation of acid to water cannot be represented by any simple formula. Indeed, it is entirely a function of the pressure under which the distillation is effected. By varying the pressure, acids of varying composition can be made to distil unchanged. At about 260° nitric acid is completely resolved into nitrogen tetroxide, water, and oxygen—



Nitric acid, as indeed its formula tells us, contains upwards of three-fourths of its weight of oxygen. It parts with a portion of its oxygen with great readiness; it is therefore an *oxidizing agent* of great power. It discharges the colour of indigo, stains the skin yellow, oxidizes phosphorus, sulphur, charcoal, and some of the metals, and converts many proto-salts into persalts. Some of these reactions may be used as *tests* for nitric acid. If a small quantity of nitre be dis-

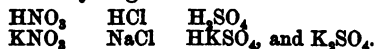
solved in a strong solution of ferrous sulphate, and a few drops of concentrated sulphuric acid be carefully poured down the side of the tube containing the solution, so that the heavy acid falls to the bottom of the tube without sensibly raising the temperature of the liquid, an immediate brown coloration will manifest itself where the two liquids meet. This effect is due to the reduction of the nitric acid, liberated by the action of the sulphuric acid, by means of a portion of the ferrous sulphate; the lower oxides of nitrogen thus produced dissolve in the remainder of the ferrous sulphate with the formation of the brown colour.

92. Definition of an Acid.—As nitric acid presents the first instance in which we have had occasion to study the properties of one of the important series of chemical compounds called the *acids*, it may now be well to state more particularly what we mean by this term.

Acids were formerly defined to be soluble substances of a sour taste (Gr. *ὄξύς*, sour; *ῥέος*, vinegar; Lat. *acidus*, sour; *acetum*, vinegar), possessing the power of reddening many blue and violet colouring matters of vegetable origin, and capable of dissolving earthy or alkaline substances with the loss of these distinctive properties. These qualities were long considered to be essential to acids, until it was recognized that many substances supposed to have no direct chemical relation to the acids also possessed these properties. Thus, common alum is soluble in water, possesses a sour taste, changes vegetable blues to red, and neutralizes the alkalinity of potash and soda.

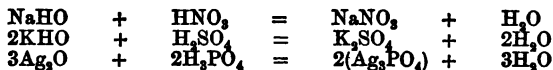
For more than a quarter of a century after the discovery by Lavoisier that many substances when burnt in oxygen gave rise to bodies possessed of the above-mentioned properties of acids, chemists were content to believe that this element was a constituent of all acids—that it was, in fact, the acidifying principle. It was pointed out, however, that many substances distinctly analogous in their relations to nitric, sulphuric and carbonic acids, and possessing acid properties, did not contain oxygen. Thus, it was shown that hydriodic, hydrochloric, and hydrocyanic acids were free from oxygen, and yet possessed the essential attributes of an acid. Hence arose the necessity of subdividing the acids into two

groups—the *oxiacids*, acids containing oxygen; and *hydracids*, acids containing no oxygen—a subdivision which is still used. After the discovery of the composition of the hydracids, Lavoisier's theory of the constitution of the acids was untenable. Davy pointed out that all the acids contained one element in common—viz., hydrogen; and Dulong, and afterwards Gerhardt, extended the observation by showing that salts might be considered to be derived from the acid by the elimination of this hydrogen. Thus—



It is evident from these relations that the constitution of acids and salts is analogous. The acids can no longer be considered as essentially distinct in their nature. They are merely particular classes of salts; they are salts of *hydrogen*. Thus, nitric acid might be fitly called hydrogen nitrate; hydrochloric acid, hydrogen chloride, and so on. Hydrogen comports itself in these compounds exactly as a metal; it leaves the *acid radicals*— NO_3 , Cl , and SO_4 —and gives place to other metallic elements, or combinations of elements, which react as metals, by a process of double decomposition.

93. Basicity of Acids.—The amount of hydrogen contained in an acid and replaceable by an element like sodium potassium or silver, determines the *basicity* of the acid. Thus, nitric acid is a *monobasic* acid; it contains only *one* atom of displaceable hydrogen. Sulphuric acid is *dibasic*, *two* atoms of potassium eliminating an equal number of hydrogen atoms from this acid. Phosphoric acid is *tribasic*; it contains *three* atoms of hydrogen which can be so replaced. Acids of a greater basicity than unity are frequently termed polybasic acids.



94. Nomenclature of Salts.—The student will already have noticed that the names of salts containing oxygen are derived from the names of the *base* and the *acid* from which they are obtained: thus, the name sodium *nitrate* indicates that this body is to be regarded as *nitric* acid in which the hydrogen has been replaced by sodium—

HNO_3	NaNO_2
Hydrogen Nitrate or Nitric Acid.	Sodium Nitrite.

Thus, too, the name sodium nitrite means that this substance is nitrous acid in which the hydrogen has been replaced by sodium—

HNO_2	NaNO_2
Hydrogen Nitrite or Nitrous Acid.	Sodium Nitrite.

It will be noticed that the acid ending in *-ous* forms a salt ending in *-ite*; and that an acid with the termination *-ic* gives salts terminating in *-ate*.

Sulphurous acid gives Sulphites.
Sulphuric acid ,, Sulphates.
Phosphorous acid ,, Phosphites.
Phosphoric acid ,, Phosphates.

95. Classification of Salts.—Salts containing oxygen are classified as *normal*, *acid*, and *basic*.

A normal salt is formed from an acid by the replacement of all its hydrogen by an equivalent amount of a metal, or by a group of elements which go in and out of combination like an element—

ACID	NORMAL SALT.
Chloric acid, HClO_3 ,.....	Potassium chlorate, KClO_3 .
Sulphuric acid, H_2SO_4 ...	{ Sodium sulphate, Na_2SO_4 .
	{ Ammonium sulphate, $(\text{NH}_4)_2\text{SO}_4$.
Nitrous acid, HNO_2 ,.....	Silver nitrite, AgNO_2 .
Phosphoric acid, H_3PO_4	Tricalcium phosphate, $\text{Ca}_3(\text{PO}_4)_2$.

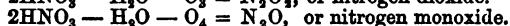
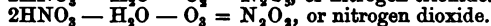
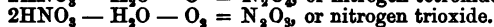
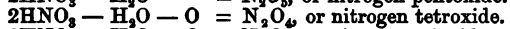
An acid salt is derived by the partial replacement of the hydrogen by a metal, or group of elements acting like a metal. Acid salts are, therefore, derived from polybasic acids—

ACID.	ACID SALT.
Carbonic acid, H_2CO_3 ,...	Sodium hydrogen carbonate, NaHCO_3 .
Sulphurous acid, H_2SO_3 ,...	Potassium hydrogen sulphite, KHSO_3 .
Sulphuric acid, H_2SO_4 ,...	Potassium hydrogen sulphate, KHSO_4 .
Phosphoric acid, PO_4H_3 {	Sodium di-hydrogen phosphate, NaH_2PO_4 .
	Di-sodium hydrogen phosphate, Na_2HPO_4 .

Basic salts are derived from normal salts by the substitution of oxygen for an equivalent amount of the acid-nucleus or *radical*; thus—

$\text{Pb}_2\text{N}_2\text{O}_5$	or	$\text{Pb}_2(\text{NO}_3)_2\text{O}_5$.
Tribasic Lead Nitrate.		
Fe_2SO_4	or	$\text{Fe}_2(\text{SO}_4)_2\text{O}_5$.
Basic Ferric Sulphate.		

96. Nitroxygen Series.—By the elimination of the elements of water, and the gradual removal of oxygen, a well defined series of nitrogen oxides may be obtained. Their relations may be thus represented—



The elimination of the water may, in the first instance, be brought about by the action of a powerful dehydrating agent. Its expulsion in subsequent cases, and the gradual withdrawal of the oxygen, may be effected by the action of various metals. The degree of deoxidation depends upon the nature of the metal, the concentration of the acid, and the temperature at which the reaction occurs.

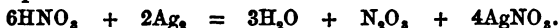
1. *Nitrogen pentoxide* may be obtained by treating nitric acid with phosphoric pentoxide—



2. *Nitrogen tetroxide* is largely formed by the action of nitric acid on tin—



3. *Nitrogen trioxide* may be obtained by the action of nitric acid upon silver—



4. *Nitrogen dioxide* is readily formed by the action of nitric acid on copper—

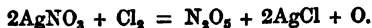


5. *Nitrogen monoxide* may be prepared by the action of zinc on dilute nitric acid—



97. Nitrogen Pentoxide.—Symbol N_2O_5 ; molecular weight 108.

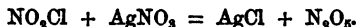
This remarkable compound was discovered by H. Deville, in 1849; he prepared it by the action of dry chlorine on perfectly dry silver nitrate. The reaction may be thus stated—



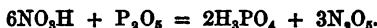
It has been shown, however, that the reaction in reality occurs in two phases. The first action of the chlorine upon silver nitrate gives rise to *nitryl chloride* (NO_2Cl), oxygen, and silver chloride—



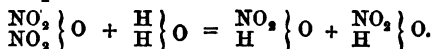
The nitryl chloride then reacts upon a second molecule of silver nitrate, forming nitrogen pentoxide and silver chloride—



Nitrogen pentoxide may be obtained by the direct action upon silver nitrate of nitryl chloride (prepared by acting on silver nitrate by phosphorus trichloride). The vapours of the nitryl chloride are passed over the well dried nitrate heated to 60° or 70° , and the nitrogen pentoxide is condensed in a tube surrounded by a freezing mixture. Nitrogen pentoxide, or nitric *anhydride* (as it is sometimes termed), may also be obtained by the *dehydration* of nitric acid by phosphoric pentoxide. To obtain it in this manner the nitric acid requires to be very concentrated and free from nitrous acid, and to be maintained perfectly cold during the reaction. The anhydride is distilled at a very gentle heat, and purified by recrystallization from strongly cooled solutions in nitric acid—



It forms colourless prismatic or needle-shaped crystals of great brilliancy, melting at 30° , and boiling at about 45° . It is a very unstable substance, slowly decomposing even at ordinary temperatures. With water it forms nitric acid—



It acts rapidly on sulphur, phosphorus, and the alkaline metals, setting them on fire. On adding it gradually to strong nitric acid, and cooling the mixture, a crystalline hydrate separates out, having the composition $2\text{N}_2\text{O}_5 \cdot \text{H}_2\text{O}$. In its chemical properties this hydrate resembles the pentoxide. It solidifies at 5° , and has a sp. gr. of 1.642 at 18° . It is slowly decomposed at ordinary temperatures, and rapidly on heating. It stands exactly in the same relation

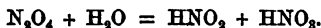
to nitric acid that Nordhausen oil of vitriol does to sulphuric acid (*infra*).

98. Nitrogen Tetroxide.— N_2O_4 or NO_2 ; molecular weight 92 or 46; density 46 or 23.

This compound may be obtained by heating well dried lead nitrate in a hard glass retort, and condensing the product in a mixture of ice and salt—



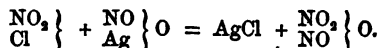
Nitrogen tetroxide forms colourless transparent crystals which melt at -10° ; when once fused they remain liquid even at -21° . This liquid, at low temperatures, is colourless, but on gently heating it acquires a faint greenish-yellow tinge; at 10° it is full yellow, at 15° orange yellow; the colour now gradually darkens with the increment of temperature up to 22° , when the liquid boils. The vapour is reddish-brown; on heating it gradually deepens in colour, and at 40° it is almost black. These remarkable changes in colour are accompanied by a rapid diminution in the density of the gas. Thus, at 26.7° its density is found to be 38.3; at 60.2° , 30.1; at 100.1° , 24.3; at 135° , 23.1. These phenomena seem to indicate the occurrence of some molecular change in the substance, resulting from the action of heat; they may be best explained by the assumption that at low temperatures the body possesses the composition, N_2O_4 , and the density 46, but that as the temperature increases its molecule gradually splits up into two molecules of NO_2 , possessing the density 23. It has been calculated that at 26.7° 20 per cent. of the molecules are dissociated; at 60.2° , 52.04 per cent.; at 100.1° , 89.23 per cent.; and at 135° , 98.69 per cent.; the dissociation being complete at about 140° . * This representation of the constitution of this compound receives some support from the reaction of water upon it at a low temperature. If a small quantity of ice-cold water be added to well-cooled nitrogen tetroxide, the following reaction occurs:—



* Dr. Andrews has recently observed a similar darkening in the colour of bromine vapour when subjected to heat; this may possibly have some relation to the phenomenon seen in the case of nitrogen tetroxide.

Nitrogen tetroxide and water form *nitrous* and nitric acids. If water at ordinary temperatures is added to nitrogen tetroxide the liquid becomes successively blue, green, and orange coloured. These changes of colour are probably due to the gradually increasing solution of the nitrogen tetroxide in the nitric acid formed.

Nitrogen tetroxide may be synthetically prepared by the action of nitryl chloride on silver nitrite—



A reaction also tending to establish for nitrogen tetroxide the formula, N_2O_4 .

Nitrogen tetroxide (NO_2) may be heated to low redness without decomposition; but strongly ignited phosphorus and charcoal decompose the gas, and burn in it with great brilliancy. Potassium inflames spontaneously in the vapour, and burns with a red flame.

99. Nitrogen Trioxide.—Symbol N_2O_3 ; molecular weight 76; density 38.

This compound is most readily prepared by the action of nitric acid of sp. gr. 1.25 upon arsenic trioxide—



Arsenic trioxide reducing the nitric acid to nitrogen trioxide and forming arsenic acid. It is red gas, fuming in the air, and condensing to a dark blue liquid at 18° . It is dissolved by water with the formation of nitrous acid, HNO_2 ; by substituting various metals for the hydrogen in this acid a series of somewhat unstable salts, termed the *nitrites*, may be obtained. The solution of this acid acts both as an oxidizing and as a reducing agent. It discharges the colour of indigo, liberates iodine from potassium iodide, and converts ferrous salts into ferric salts. On the other hand, it reduces permanganic and chromic acids to lower states of oxidation, and eliminates gold and mercury in the metallic state from their combinations.

The production of ammonium nitrite from water and atmospheric nitrogen has already been mentioned. Still

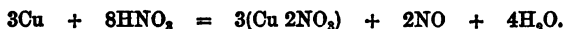
larger quantities of this compound are obtained by burning hydrogen in the air; the condensed water will be found to give readily the reactions of nitrous acid.

A very instructive illustration of the formation of ammonium nitrite may be witnessed by plunging a thick coil of platinum wire, heated to redness, into an atmosphere of ammonia, created by pouring a few cubic centimetres of strong ammonia solution into a flask. The platinum continues to glow with increased energy, and white fumes of ammonium nitrite are formed. By allowing a gentle stream of oxygen to pass into the ammoniacal solution, the action will be augmented. Occasionally the temperature of the platinum becomes so high that an explosion results.

Nitrites are not unfrequently found in the well waters of towns; they have in such cases been formed by the oxidation of nitrogenous organic matter due to the infiltration of sewage into the waters.

100. Nitrogen Dioxide.—Symbol NO; molecular weight 30; density 15.

This gas is usually prepared by the action of nitric acid upon copper. The reaction has already been represented—



The nitric acid should be diluted with its own volume of water; if the temperature is allowed to rise, or if stronger acid be employed, the gas becomes mixed with free nitrogen and nitrogen monoxide. It may also be abundantly obtained in a purer state by heating a solution of ferrous sulphate, acidulated with sulphuric acid with potassium nitrate—



Nitrogen dioxide is a colourless permanent gas, of sparing solubility in water. It is abundantly soluble in nitric acid, to which it imparts a brown, green, or blue colour, varying with the concentration of the acid. These changes are probably due to its conversion into nitrogen tetroxide. The gas is also freely dissolved by ferrous sulphate solution, to which it imparts a deep brown colour; the formation of this colour is employed as a test for nitric acid.

Nitrogen dioxide readily combines with oxygen, with the formation of dense red fumes, consisting for the most part

(particularly if the latter gas be in excess) of nitrogen tetroxide. As these fumes are immediately dissolved by water, it is possible, by means of nitrogen dioxide, both to detect the presence and to determine the amount of free oxygen in a mixture of gases. This method was formerly much used as an eudiometric process: it was so employed by Priestley and Cavendish.

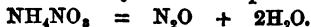
Nitrogen dioxide is a feeble supporter of combustion. Although it contains nearly three times the amount of oxygen which is present in the same bulk of air, it extinguishes a lighted taper, and the flame of burning sulphur. Phosphorus, when rapidly burning, is able to decompose the gas, and so continues to burn in the liberated oxygen. Nitrogen dioxide and carbon bisulphide vapour form a highly inflammable mixture, which burns with an almost instantaneous flash of lavender coloured flame.

Nitrogen dioxide is the most stable of the oxides of nitrogen. It is not decomposed at a low red heat, and is but slowly resolved into its elements by the induction spark. Nitrogen dioxide mixed with hydrogen and passed over heated platinum black is converted into ammonia.

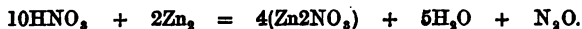
One litre of nitrogen dioxide at the standard temperature and pressure is found to weigh 1.343 grams. It is therefore $\frac{1.343}{0.0896}$, or 15 times heavier than hydrogen. Its composition may be ascertained by heating potassium in a measured volume of the gas; the potassium deflagrates, and the residual gas is found to be pure nitrogen; it occupies half the original volume. Two volumes of nitrogen monoxide, weighing 30, are made up of 1 volume of nitrogen, weighing 14, and 1 volume of oxygen, weighing 16, united without condensation. Hence the formula of the gas is NO, and not N₂O₂, which analogy and its place in the series of nitroxygen compounds might seem to indicate. Possibly when the gas is condensed it may be found that its molecule, as in the case of the tetroxide, possesses twice the ordinary weight.

101. Nitrogen Monoxide.—Symbol N₂O; molecular weight 44; density 22.

This gas may be prepared by heating ammonium nitrate NH₄NO₃; the reaction may be thus represented—



Ammonium nitrate forms nitrogen monoxide and water. Care should be taken not to heat the salt above 250° , otherwise a portion of the gas is resolved into nitrogen and nitrogen dioxide. Ammonium nitrate, and nitrite sublime and free ammonia is generated. This decomposition is occasionally attended with an explosion. The gas may also be obtained by the action of dilute nitric acid upon zinc—



It is likewise formed by decomposing nitric acid by means of a solution of stannous chloride in hydrochloric acid; by heating sal-ammoniac with dilute nitric acid (sp. gr. 1.2); and by passing a slow stream of nitrogen dioxide into sulphur dioxide solution.

Nitrogen monoxide is a colourless gas, of a faint odour and sweetish taste. It is slightly soluble in water; 100 volumes of water absorb 130 volumes of the gas at 0° , and 61 volumes at 24° . In collecting it over the pneumatic trough warm water should therefore invariably be used. If cooled down to -88° , or exposed to a pressure of 30 atmospheres at 0° , it condenses to a mobile liquid of sp. gr. 0.908: according to Faraday it is the least refractive of all liquids. In contact with the skin it produces a blister like a burn; potassium floats on its surface unaltered; sulphuric and nitric acids and water are immediately frozen when mixed with it. By cooling the liquid to -115°C ., or by allowing it to evaporate very rapidly, it may be frozen to a white snow-like mass. When mixed with carbon bisulphide in vacuo it produces the lowest temperature hitherto attained—viz., about -140° . Liquid nitrogen monoxide may be readily obtained by compressing the gas by mechanical means. Fig. 71 shows the iron or copper receiver into which it is compressed by means

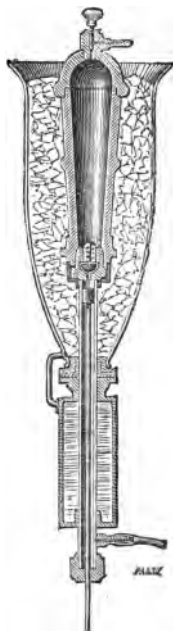


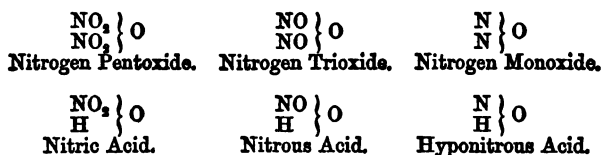
Fig. 71.

of a force pump. In order to facilitate the condensation the vessel is cooled by immersion in a mixture of ice and salt.

Nitrogen monoxide, although containing less oxygen than the dioxide, is a far more energetic supporter of combustion than that substance. A glowing chip of wood bursts into flame when plunged into the gas, and phosphorus, sulphur, zinc, and iron burn with almost as much brilliancy as in pure oxygen, to form their respective oxides. Sodium or potassium heated in the gas burns with the formation of an alkaline monoxide. This reaction may serve to determine the composition of nitrogen monoxide. After deflagration, the residual nitrogen is found to occupy the original volume of the gas. As the gas is found by experiment to have the density 22, two volumes of it must be made up of two volumes of nitrogen combined with one volume of oxygen condensed to two volumes. Accordingly its formula is N_2O .

Nitrogen monoxide exerts a very remarkable action on the economy when breathed. Inspired in small quantity it occasions a transient form of intoxication, which quickly passes into complete insensibility. On account of the ease and certainty with which this latter effect may be produced, nitrogen monoxide has received an important application as an anæsthetic agent, particularly in minor surgical operations. Its action is very brief, and without injurious or disagreeable after-effects, if the gas be free from other oxides of nitrogen.

Nitrogen monoxide appears to give rise to an acid which stands in exactly the same relation to this gas that nitrous and nitric acids respectively stand to nitrogen trioxide and pentoxide. This acid has the formula HNO ; it may be called *hyponitrous acid*—



The sodium salt of the new acid, $NaNO$, is obtained by digesting a cold solution of sodium nitrate with sodium amalgam. If the alkaline liquid be neutralized with acetic

acid, and mixed with silver nitrate solution, a yellow pulverulent precipitate of silver hyponitrite, AgNO , is formed. (*Divers Proc. Roy. Soc. 1871.*)

102. Hydroxylamine.—Symbol NH_2OH .

This remarkable substance may be obtained by the action of nascent hydrogen upon nitrogen dioxide. If a stream of nitrogen dioxide be passed into a series of flasks containing tin and hydrochloric acid mixed with a small quantity of platinum tetrachloride solution (whereby hydrogen is evolved at the ordinary temperature), the chloride of the new base is formed. It may be obtained by freeing the solution from tin by a current of sulphuretted hydrogen, filtering and evaporating to dryness. The saline mass is first washed with cold alcohol, and then boiled with absolute alcohol to dissolve the hydroxylamine chlorides. By adding a little ether to the solution, the chlorides are precipitated in small crystals, which may be purified by recrystallization from absolute alcohol.* The salts of this base are all highly soluble crystalline compounds; they are free from water of crystallization, and are decomposed at a gentle heat. The base itself is known only in solution; it is very volatile, and is easily decomposed; it possesses an alkaline reaction, and precipitates solutions of lead, iron, nickel, and zinc. With solution of copper sulphate it forms a light green precipitate which is reduced to cuprous oxide on heating with water.

CHAPTER IX.

103. Carbon.—Symbol C ; atomic weight 12.

The study of this element, strictly speaking, belongs to the division of Organic Chemistry, or that portion of the science which treats of the carbon compounds. But carbon possesses

* Lossen has recently shown that a number of these chlorides exist. He has obtained the following:— $\text{NH}_2\text{O} \cdot \text{HCl}$, $2\text{NH}_2\text{O} \cdot \text{HCl}$, and $3\text{NH}_2\text{O} \cdot 2\text{HCl}$. The two latter salts are deliquescent, and very sparingly soluble in alcohol.

such important relations to the other elements that it is absolutely necessary, even at this early stage of our study of Inorganic Chemistry, to consider its main properties, together with those of some of its combinations with hydrogen, oxygen, nitrogen, &c.

Carbon is one of the most widely diffused of the elements. It occurs in the free state as the diamond, as graphite, and as charcoal; these three varieties constitute *allotropic modifications* of the element. No better example of the striking differences which it is possible to effect in the physical appearance of a substance, by variety of atomic arrangement, could be adduced than that of the allotropes of carbon.

Carbon also exists in nature in combination with oxygen, forming carbon dioxide, a gas which is present in the free state in the air, and is largely evolved from subterranean sources. A large proportion of the solid crust of the earth is made up of compounds of carbon dioxide with various bases, entire mountain chains being composed of the carbonates of calcium and magnesium. Immense areas of calcium carbonate, brought together by the vital processes of minute organisms, exist beneath the sea's surface. All organic matter contains carbon in union with hydrogen, oxygen, nitrogen, &c.; indeed, this element is specially characteristic of animal and vegetable life; every organism contains it. Carbon enters into the composition of a large number of compounds than any other element. Its combinations with hydrogen are particularly numerous; the petroleum oils, naphtha, marsh-gas, benzene, illuminating gas, &c., are all *hydrocarbons*—that is, compounds of carbon and hydrogen.

104. The **Diamond** is the purest form of carbon; when colourless it leaves after combustion only a minute trace of earthy matter. Diamonds are not unfrequently found of a yellow, red, green, brown, or black colour; their colour is generally due to mineral matter. Such diamonds when burnt leave from 0.2 to 0.6 per cent. of ash.

The diamond is found in various parts of the world, particularly in India, Brazil, Borneo, and South Africa. Although the other forms of carbon are very abundant in Great Britain, the diamond has never been discovered in these islands; indeed there is only a single instance of its

having been found in Europe—viz., in Bohemia. - The mode in which the diamond is formed is quite unknown to us.

The diamond was first shown to be a combustible substance by the members of the Academy del Cimento, who succeeded in burning it by the aid of a lens. Lavoisier found that the sole product of its combustion in oxygen was carbon dioxide. The diamond (*adamant*) is one of the hardest substances known; it is capable of scratching and cutting the greater number of other bodies. It is largely used for cutting glass and for polishing gems. The abrasion of the diamond itself can only be effected by its own dust. The diamond occurs in well defined crystals belonging to the regular system; some of its forms are highly complicated. Its specific gravity is about 3.5. Under ordinary circumstances it is perhaps the most unchangeable of all substances, but in the intense heat of the electric arc it swells up, and is converted into a black opaque mass of coke.

105. **Graphite** is found in formations in which the diamond has not yet been discovered. It occurs in Cumberland, in Cornwall, and in various parts of Scotland, Ireland, and the Isle of Man. It is also found in Ceylon, and in the United States, &c. It usually occurs in massive or in hexagonal plates, crystallizing in a form totally distinct from that of the diamond. Carbon is therefore *dimorphous*—i.e., it occurs in two distinct crystalline shapes. Graphite has a well known leaden-gray lustre (hence its common name of black-lead); it is friable, and leaves a streak on paper, whence its application in the manufacture of lead pencils. Its specific gravity is about 2.2. It always contains more or less admixed earthy matter. Unlike the diamond, it is a good conductor of electricity; hence its application in the electrolytic process. Its friability renders it valuable as a lubricant for machinery and for polishing stoves; and its permanency leads to its employment in the manufacture of crucibles, and as a covering for the surface of gunpowder.

Carbon in the form of graphite occasionally separates out from molten cast iron; the peculiar colour and appearance of gray cast iron are due to the dissemination of particles of graphite or "kish" throughout the mass of metal. Graphite has also been observed to form in the decomposition of

alkaline cyanides. The mother liquors obtained in the manufacture of soda-ash are often utilized to make caustic soda. For this purpose it is necessary to oxidize the sulphides and cyanides contained in them; sodium nitrate is therefore added, and the whole is evaporated to dryness and heated, when the surface of the mass is observed to become covered with a layer of graphite.

Graphite requires the action of the strongest agents to oxidize it. By a process of limited oxidation it is converted into a crystalline substance, termed *graphitic acid* by Brodie, its discoverer. This body has the composition $C_{11}H_4O_5$. Schulze has recently made the interesting observation that graphite may be oxidized to *mellitic acid* $C_6H_2O_4$, an acid occurring naturally in honeystone or mellite (aluminium mellitate).

106. Charcoal is distinguished from the preceding modifications of carbon by its want of regular geometrical form; it is accordingly termed the *amorphous* variety of carbon. Charcoal is readily obtained by the destructive distillation of organic substances. Wood, for example, when heated out of contact with air, yields a variety of volatile products, and leaves a residue of charcoal. This charcoal is not pure carbon; it always contains oxygen, hydrogen, and a small quantity of nitrogen, in addition to the mineral constituents or ash of the wood.

Where wood is plentiful, it is often converted into charcoal by burning it with a very limited supply of air; the combustion of a portion of the wood is made to effect the carbonization of the rest. Billets of wood are built into a large conical heap, which is carefully covered over with turf, or moistened ashes obtained from previous burnings; holes are left at the base of the heap, together with a hollow space in the centre. Through the latter lighted faggots are thrown, which set up the slow combustion of the whole mass, the gaseous matters being evolved through the centre flue, and through the holes at the bottom. The operation of burning requires careful watching; it lasts for several days, and yields about 24 per cent. by weight of charcoal.

In this country, where the volatile matters are of more importance than the charcoal, the wood is heated in large

iron cylinders; among the products of its destructive distillation are found tar, pyroligneous acid (acetic acid), and wood spirit.

Charcoal swims on the surface of water. In reality, however, it is specifically heavier than that liquid, its specific gravity being about 1.5; its apparent lightness is due to the buoyant action of the air inclosed within its numberless pores. The highly porous nature of charcoal may be rendered evident by sinking it (by means of an attached piece of lead) in a cylinder of water, and placing the cylinder under the receiver of an air-pump; on exhausting the air, a number of bubbles will start from the surface of the charcoal, and give the liquid the appearance of effervescence. The same fact may be elegantly shown by the aid of the apparatus seen in fig. 72. The tall, cylindrical glass vessel *a* is completely filled with water, and, before the cover is screwed down, a few pieces of charcoal are placed on the surface of the liquid. By alternately turning the three-way cock *s*, communication may be effected either with the vessel *a*, or with the reservoir *b*; and, by raising and depressing the piston *c*, water may be forced into the cylinder. The compression experienced by the water is determined by the contraction seen in the air-gauge *d*; as soon as it reaches 3 or 4 atmospheres, the pieces of charcoal will be observed to sink. The air within the pores is compressed to such a degree that water enters, and thus renders the mass specially heavier than the liquid. On gradually turning the cock, so as to allow the compressed water to flow back into the reservoir, the air within the manometer will expand, and the charcoal will rise again to the surface.

By virtue of its porosity, charcoal readily absorbs gases.

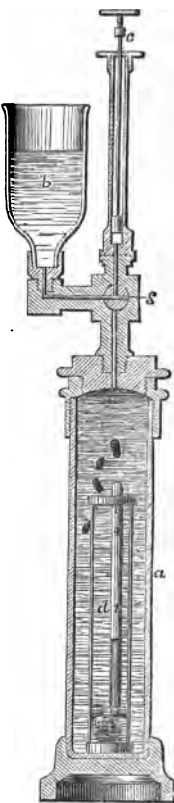


Fig. 72.

If a piece of recently ignited charcoal be brought into a tube containing ammonia gas, and standing over mercury, the gas will be rapidly absorbed, and the mercury will rise in the tube. If a fragment of charcoal be heated, and allowed to cool in an atmosphere of sulphuretted hydrogen, and be then plunged into a jar of oxygen, it will burst into flame, owing to the energy of the mutual action of the gases. Charcoal from hard wood absorbs gases to the greatest extent. Of the various forms of charcoal, the best absorbent appears to be that obtained from the shell of the cocoa-nut. One volume of such charcoal ignited and quenched under mercury absorbs, at the ordinary temperature, the following volumes of the various under-mentioned gases (measured at 0° and 760 m.m.):—

Ammonia,.....	171·7 vols.	Hydrogen phosphide, 69·1 vols.
Cyanogen,.....	107·5 „	Carbon dioxide, 67·7 „
Nitrogen dioxide, .	86·3 „	Carbon monoxide, 21·2 „
Ethene,.....	74·7 „	Oxygen, 17·9 „
Nitrogen monoxide, 70·5 „		

Vapours are also absorbed by charcoal in amount varying with the temperature. The volume absorbed decreases as the vapour is more and more removed from its point of condensation. This fact will be seen from the following table. The absorbent in all cases was cocoa-nut charcoal :*—

	Volume Absorbed.	Temperature.
Ammonia,	21·9	126·2
Carbon dioxide,	16·6	126·5
Steam,	43·8	127·5
„	23·7	158·8
Alcohol,	145·8	89·5
„	141·1	100·0
„	110·8	126·5
„	83·4	158·7

The gas expelled from charcoal which has remained exposed to the air for a long time, consists entirely of nitrogen and carbon dioxide: the oxygen absorbed at the same time as the nitrogen having become converted, by contact with the carbon, into carbon dioxide. In consequence of its power of absorbing gases, charcoal is largely used as a

* Hunter, *Chem. Soc. Journ.* [2], III. 285, V. 160, VI. 189.

disinfectant. The fetid and deleterious gases evolved in putrefaction are immediately absorbed by powdered charcoal, and oxidized by the oxygen condensed within its pores. When sprinkled over decomposing organic matter all effluvium is at once arrested by the powder. For this reason the ventilating shafts of sewers are fitted with cases containing charcoal. The respirators invented by Dr. Stenhouse constitute a valuable application of this property of charcoal.

The various forms of charcoal have also received very extensive applications in the arts from their power of decolorizing liquids. If recently ignited and powdered charcoal be heated with a decoction of logwood, the colour of the liquid will be discharged. This power of decolorization is possessed in a much higher degree by **animal charcoal** or **bone-black**, the substance obtained by charring bones in closed vessels. The composition of bone before and after charring may be thus represented—

Before Charring.		After Charring.	
Organic matter,	30.0	Carbon,	10.0
Calcium phosphate,	60.2	Calcium phosphate,	88.0
Magnesium phosphate and calcium carbo- nate, &c.,	9.8	Other salts,	2.0
	100.0		100.0

Bone-black is simply a highly porous mass of calcium phosphate containing finely disseminated carbon. It is employed to a large extent in decolorizing syrups in sugar refining; its application to this purpose was proposed by Derosnes in 1812. The charcoal in coarse powder is placed in long cylinders varying in depth from 10 to 50 feet, and the dark brown syrup is run on to it from the filters. The saccharine fluid issues from beneath in a perfectly colourless stream. The consumption of charcoal in a sugar refinery is very large, about one ton of charcoal being required to purify a ton of sugar. After a time the charcoal loses its power of decolorizing, but by washing and reheating in closed vessels it may be *revivified*.

Bone-black absorbs various substances when agitated with their solutions. Thus, it abstracts lime from lime water, and lead acetate from its solutions; it even separates iodine from

potassium iodide. Its power of abstracting lime is found to stand in some relation to its decolorizing property: a method of determining the value of animal charcoal for the purposes of the sugar refiner is based on the estimation of the amount of lime which the sample can absorb. The charcoal obtained by the carbonization of sea weeds also possesses a marked decolorizing action.

Bone-black is used to some extent as a pigment. Large quantities of carbon, under the form of **lamp-black**, formed by the imperfect combustion of tallow, oil, or pitch, are also used for the same purpose. These substances, particularly pitch or resin, are heated, and the ignited vapours, mixed with an amount of air insufficient for complete combustion, are led into a chamber, in which the soot is deposited. Lamp-black so prepared always contains oily matter, from much of which it may be purified by ignition in covered crucibles; but even after prolonged heating it retains a considerable amount of hydrogen.

107. Coal is essentially carbon combined with hydrogen, oxygen, and nitrogen, and more or less mineral substance. It has been produced from vegetable matter by a complicated series of chemical changes, attended with the elimination of water, carburetted hydrogen, and carbon dioxide. Its vegetable origin is established by its ligneous structure, and by its association with the fossil remains of the flora from which it has been derived. The gradual transition of woody fibre to anthracite or stone coal is well seen in the following table:—

	Carbon.	Hydrogen.	Oxygen and Nitrogen.
(1.) Oak-wood,	50·17	6·08	43·75
(2.) Decayed oak,	53·47	5·19	41·34
(3.) Peat (Irish),	60·05	5·88	34·10
(4.) Lignite (Bovey),	69·54	5·89	24·56
(5.) Cannel (Wigan),	83·59	5·77	10·64
(6.) Caking coal (Newcastle),	87·98	5·31	6·71
(7.) Anthracite (South Wales), ...	92·73	3·36	3·91

All coals contain inorganic matter or ash, varying in quantity from 1 to 30 per cent. In good bituminous coal the amount should not exceed 10 per cent. The ash usually consists of silicates of alumina and iron. The composition of the

ash of Scotch coal may be thus stated (average of five samples)—

Silicia.	Alumina and Ferric Oxide.	Lime.	Magnesia.	Sulphuric Acid.	Phosphoric Acid.
49·63.	38·21.	3·18.	1·41.	6·26.	1·03.

A portion of the sulphuric acid is probably derived from the oxidation of iron pyrites, which is generally present in coal to the amount of three per cent., although some coals contain much larger quantities of this substance. The amount of sulphur which it contains has an important bearing on the value of the fuel in nearly all its applications. When the coal is burnt the sulphur escapes as sulphur dioxide. This gas exerts a very detrimental action on vegetation, and by its proneness to pass into the state of sulphuric acid in the atmosphere it brings about the rapid deterioration of the stone-work on which it may be precipitated. It has been calculated that as much as 20 tons of oil of vitrol, produced by the combustion of coal, are annually brought down by the rain in a large city like Glasgow or Manchester. The sulphur in coal also exerts a prejudicial effect in iron smelting and in the manufacture of coal gas; and it rapidly acts on boiler plates, locomotive tubes, &c.

108. Compounds of Carbon and Hydrogen.—The hydrocarbons constitute the most extensive class of compounds known to the chemist. Although it is almost impossible even now to enumerate those which have already been described, we are certain that by far the larger number of the possible combinations of carbon and hydrogen have still to be discovered. Some of the hydrocarbons are gaseous, like those we are about to describe; some, as benzine, the petroleum oils, &c., are liquid at ordinary temperatures, whilst others, like paraffin and anthracene, are solid. For our present purpose it is necessary to direct particular attention to three only of these compounds, namely:—

Methane or Marsh Gas,	-	-	CH_4	-	mol. wt. 16
Ethene or Ethylene,	-	-	C_2H_4	-	„ 28
Ethine or Acetylene,	-	-	C_2H_2	-	„ 26

Each of these bodies constitutes the starting point or first

in the proportion of pairs of hydrogen atoms, is termed an **isologous series**. Thus, the compounds ethane, ethene, and ethine constitute such a series—



All the compounds of carbon and hydrogen at present known to us are included in the following twelve homologous series:—

$\text{C}_n \text{H}_{2n+2}$		$\text{C}_n \text{H}_{2n-10}$
$\text{C}_n \text{H}_{2n}$		$\text{C}_n \text{H}_{2n-12}$
$\text{C}_n \text{H}_{2n-2}$		$\text{C}_n \text{H}_{2n-14}$
$\text{C}_n \text{H}_{2n-4}$		$\text{C}_n \text{H}_{2n-16}$
$\text{C}_n \text{H}_{2n-6}$		$\text{C}_n \text{H}_{2n-18}$
$\text{C}_n \text{H}_{2n-8}$		$\text{C}_n \text{H}_{2n-24}$

109. Methane (*Methyl Hydride, Marsh Gas, Light Carburetted Hydrogen*).—Symbol CH_4 ; molecular weight 16; density 8.

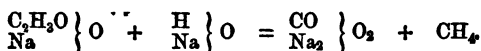
Of all the compounds of hydrogen, methane contains the largest amount of that gas. It contains as much as 25 per cent. of hydrogen, to which gas it bears considerable resemblance. It is eight times heavier than hydrogen, and is therefore the next lightest body known. It is colourless, tasteless, and inodorous, and has not yet been condensed to the liquid state. It burns with a feebly illuminating flame, and, when mixed with air or oxygen, explodes violently on the approach of a light. It is very slightly soluble in water and alcohol; 100 vols. of water at 0° dissolving 5.4 vols. of the gas.

Methane is very abundant in nature. It has already been mentioned that it is one of the gaseous products formed in the conversion of wood into coal. It is therefore very frequently met with in the coal measures. Fire-damp, as the gas is called by the miners, is the source of the explosions which too often occur in coal pits. When recently raised, coal always contains occluded gas; 100 grams of coal will give off 200 c.c. of gas, principally consisting of methane. The following analysis shows the composition of the gas enclosed by Durham coal taken 148 fathoms below the surface:—

CO_2	CH_4	O	N	
0.23	89.61	0.55	9.61	= 100.00.

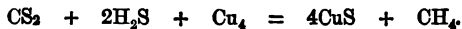
Methane is abundantly disengaged in marshy districts (whence its name of marsh gas); it is produced by the decay of submerged vegetable matter, and may be frequently observed rising to the surface of stagnant water covering organic matter.

The readiest method of obtaining the gas artificially consists in heating an alkaline acetate with potassium or sodium hydroxide. The reaction in the case of sodium acetate is as follows:—



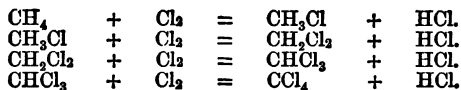
In practice the materials are mixed with quicklime, which facilitates the operation. The mass requires to be strongly heated before the gas is disengaged.

Methane may also be obtained synthetically by passing the vapour of carbon bisulphide mixed with hydrogen sulphide over red hot copper—



Other methods of producing this gas are mentioned in the volume on *Organic Chemistry*.

Methane is an exceedingly inert substance; it resists the action of the most potent reagents. This stable character it shares in common with the other members of the $\text{C}_n\text{H}_{2n+2}$ series, whence the generic name of *paraffins* (from *parum affinitatis*), which is sometimes given to the group. By the action of chlorine in bright daylight, a series of *substitution products* are obtained from methane, the chlorine taking the place of the hydrogen by successive replacement of its atoms—



110. Ethene (*Ethylene, Olefiant Gas, Ethyl, Etherin, Heavy Carburetted Hydrogen*).—Symbol C_2H_4 ; molecular weight 28; density 14.

This compound may be obtained by the dry distillation of

many organic substances; wood and coal, when heated in closed vessels, produce it in considerable quantities. It is a constituent of coal gas, the illuminating power of which is mainly due to the ethene which it contains. It may be obtained by a variety of chemical reactions, but the simplest method of preparing it consists in abstracting the elements of water from ordinary alcohol—



A mixture of 1 volume of strong alcohol and 4 volumes of sulphuric acid readily yields ethene when gently heated. Great care is necessary to prevent the liquid frothing; if too strongly heated the mixture is apt to blacken considerably, when sulphur dioxide is liberated. A far better method of conducting the process is to mix alcohol vapour with moderately concentrated sulphuric acid heated to 160° ; the sulphuric acid does not blacken, and no evolution of sulphur dioxide occurs. The apparatus represented in fig. 73 may be

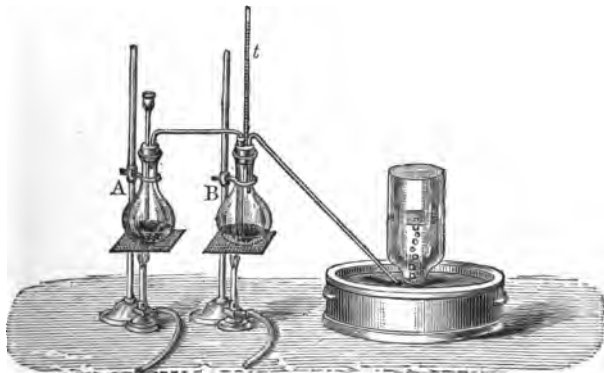
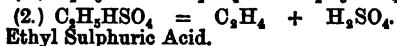
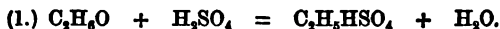


Fig. 73.

conveniently employed to prepare the gas. The flask A contains ordinary spirits of wine; B contains 10 parts of oil of vitriol, diluted with 3 parts of water. The acid is maintained at 160° — 165° , the temperature being ascertained by the thermometer *t*. Although the action ultimately consists in the dehydration of the alcohol, it is probable that the first

effect of the sulphuric acid is to convert the alcohol into ethyl-sulphuric acid, which is subsequently split up into ethene and sulphuric acid—



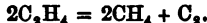
Ethyl Sulphuric Acid.

Other dehydrating agents may be used instead of sulphuric acid. Thus, boric anhydride heated with absolute alcohol produces very pure ethene.

Ethene is a colourless gas. As ordinarily prepared it contains more or less ether vapour, which communicates an odour to it. It cannot be respired. It is very sparingly soluble in water. Under strong pressure, and at a temperature of -110° , it condenses to a thin mobile liquid. When heated strongly it is decomposed, yielding ethane and ethine—



At a higher temperature it is decomposed into marsh gas and free carbon—

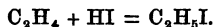


When inflamed, ethene burns with a bright white flame, possessed of considerable illuminating power. In the combustion the gas is probably first decomposed in the manner above represented, the ethane, ethine, and methane being further decomposed, the carbon and hydrogen eventually burning to carbon dioxide and water. When only moderately heated it yields among other products polymers of ethine—viz., benzene, cinnamene, &c. (*vide infra*). Ethene rapidly combines with chlorine and bromine, forming *addition products*; one molecule of the hydrocarbon uniting directly with two atoms of the halogen—

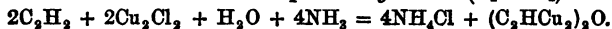


These compounds are heavy, oily, aromatic liquids; whence the name *olefiant* gas, by which ethene is sometimes designated. Ethene is quickly absorbed by fuming sulphuric acid and sulphur trioxide. The former substance is sometimes employed to determine the proportion of ethene and its congeners in coal gas. The homologues of ethene are also

absorbed by this reagent; the contraction experienced by a known volume of coal gas in contact with fuming sulphuric acid affords a measure of its illuminating power. Ethene, when continuously agitated with sulphuric acid, yields ethyl-sulphuric acid; if the acid solution be then diluted with water and distilled, ordinary (ethyl) alcohol is obtained. An alkaline and well cooled solution of potassium permanganate, when agitated with ethene, yields carbonic, formic, and oxalic acids. When heated with hydriodic acid ethene yields ethyl iodide, from which ethyl alcohol may also be prepared—



111. Ethine (*Acetylene*, *Klumene*).—This hydrocarbon may be synthetically formed by intensely heating carbon in an atmosphere of hydrogen. A voltaic discharge is passed between carbon poles connected with a powerful battery; when the carbon is heated to whiteness it is surrounded with hydrogen, whereby combination of the elements is effected. Ethine is one of the most stable of carbon compounds; it is formed under circumstances in which no other combination of the element can exist. The incomplete combustion of most organic compounds gives rise to ethine; ether, for example, passed through a red hot tube produces large quantities of the gas. Ethene and marsh gas, when strongly heated, are also decomposed into ethine and hydrogen. This decomposition of these gases constitutes one of the most convenient sources of this compound. If the flame of the Bunsen lamp be caused to burn in the interior of the tube, a disagreeably smelling gas is produced, consisting in great part of ethine. Its presence among the products of the imperfect combustion of the hydrocarbons of coal gas may be demonstrated by inverting a flask over the tube for a few minutes, and quickly pouring into it an ammoniacal solution of cuprous chloride, when the sides of the flask will become covered with a red film of *cuprosovinyll oxide* (C_2HCu_2)²O—



Considerable quantities of this compound may be easily prepared by means of the apparatus represented in fig. 74. A lamp cylinder or *adapter* is fitted at its narrow end with a cork and bent-tube, *c*, which is connected with a supply

of coal gas. The lower opening is also fitted with a cork, carrying two tubes, *a* and *b*; *a* is of brass, and is about 15 m.m. wide, and 12 c.m. long; *b* is of glass, and is connected with a *separating funnel* in the manner represented in the figure. The lower opening of the tube is closed by a cork, through which passes a tube, *c*, connected with a gas holder containing atmospheric air. Coal gas is allowed to flow through the tube *e*, and when all the air is expelled from

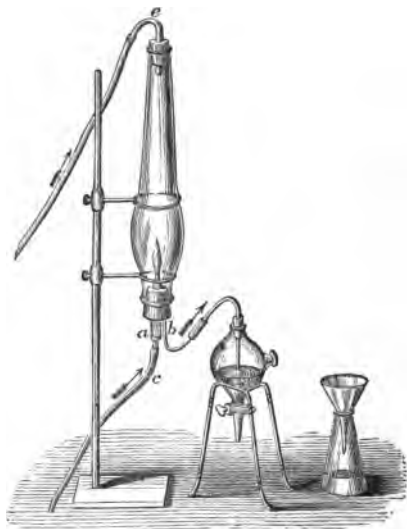


Fig. 74.

the apparatus, the cork at the bottom of the tube *a* is withdrawn, and a light is applied to the end. The current of gas is so regulated that it burns with a small flame at the opening. A gentle stream of air is then caused to pass from the gasometer, and the tube is pushed up through the flame into the cylinder. The air now burns in the coal gas; the flame may be rendered more visible by attaching a piece of platinum wire to the tube, which becomes heated to redness. The products of combustion pass through the tube *b*, and

are led into the separating funnel, which is partially filled with an ammoniacal solution of cuprous chloride; cuprosovinyl oxide is abundantly formed: when the copper solution is exhausted the liquid is allowed to flow on to a filter by opening the stop cock. A fresh quantity is poured into the funnel, and the process of absorption is recommenced.*

The formation of ethine by the action of heat on ethene may be readily shown by means of the simple arrangement seen in fig. 75. The tube *a* is connected with a gasometer

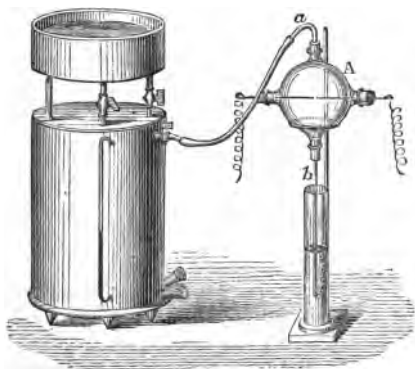


Fig. 75.

filled with ethene; the gas is allowed to flow in the four-necked globe *A*; by means of the wires, a succession of

* The solution of cuprous chloride may be readily obtained by dissolving 10 grams of cupric oxide in 200 c.c. of hydrochloric acid; and boiling the solution for about 15 minutes with 28 grams of metallic copper in filings. The solution of the cuprous chloride is poured into about a litre of water, the precipitated chloride is allowed to subside, and the liquid is drawn off. The precipitate is rinsed into a bottle of 150 c.c. capacity, which is filled up with water, and the precipitate is again allowed to subside. The supernatant liquid is removed by a syphon, and about 40 grams of powdered ammonium chloride is added to the bottle, which is again filled with water, and briskly agitated. When required for use the liquid is mixed with one-tenth of its volume of strong ammonia solution. The solution should be free from cupric salts, since these bring about the oxidation of the ethine, and prevent the formation of the red precipitate.

electric sparks can be passed through the gas. The tube δ dips beneath an ammoniacal solution of cuprous chloride; on passing the gas between the spark stream, an immediate production of the red cuprosovinyl oxide is observed.

The red compound, treated with strong hydrochloric acid, is immediately decomposed, and ethine is disengaged. $(C_2H\ Cu)_2O + 4HCl = 2\ Cu_2Cl_2 + H_2O + 2\ C_2H_2$. As the gas is somewhat soluble in water, it is best collected in a small gas-bag. Cuprosovinyl oxide, when dry, is an exceedingly unstable substance; very slight causes, gentle heating or even friction, being sufficient to decompose it with explosion. Ethine is an invariable constituent of coal gas. Its presence therein may be readily demonstrated by the formation of the red precipitate when a stream of the gas is allowed to pass through a U tube containing a small quantity of ammoniacal solution of cuprous chloride. It has been supposed that the dangerous explosions which occasionally occur when a copper gas-main is cleaned out after long use, may be due to the decomposition of cuprosovinyl oxide. Ethine mixed with air, especially in presence of aqueous vapour, rapidly attacks copper with the formation of cuprosovinyl oxide and copper oxide; at a gentle heat, or by friction, the combination is decomposed with explosion. Similar compounds with silver, gold, and mercury have been obtained. When gently heated with sodium, part of the hydrogen is eliminated, the alkaline metal taking its place, forming monosodium-ethine, C_2HNa . If more strongly heated, both the atoms of hydrogen are displaced with the formation of disodium-ethine, C_2Na_2 . The corresponding potassium compound is sometimes found in the commercial metal.

Ethine is a colourless gas, possessing a peculiar and disagreeable odour. It is irrespirable and poisonous, combining with the hæmoglobin in the blood. It is somewhat lighter than air, being thirteen times heavier than hydrogen. It has not yet been condensed to the liquid state. When inflamed, it burns with a bright smoky flame. If strongly heated, or if a series of induction sparks are passed into the gas, it is decomposed with separation of carbon. The decomposition is retarded by mixing it with other gases, particu-

larly with hydrogen. This explains why ethine is formed at the high temperature of the electric arc in spite of its tendency to resolve itself into carbon and hydrogen.

The action of heat on ethine is remarkable from the ease with which the gas is converted into its polymerides. If heated to dull redness in a tube standing over mercury, it is almost entirely resolved into mixtures of hydrocarbons, having the same per centage composition, but possessing different molecular weights. The following substances have thus been actually obtained:—

Di-ethine,	C_4H_4
Tri-ethine (benzene),	C_6H_6
Tetra-ethine (styrol),	C_8H_8
Penta-ethine,	$C_{10}H_{10}$
Enne-ethine,	$C_{18}H_{18}$

This reaction is interesting, as constituting a means of synthetically forming a number of organic compounds in the simplest manner possible, and affords additional evidence to us of the irrational character of the division of the science into organic and inorganic chemistry. Nascent hydrogen converts ethine into ethene. If cuprosoviny oxide be treated with zinc and aqueous ammonia (which evolves hydrogen), ethene is disengaged. By the action of finely divided platinum a still larger quantity of hydrogen may be made to unite with the gas. If a small quantity of platinum black be introduced into a mixture of ethene and hydrogen, standing over mercury, the gases combine in the proportion of 1 vol. of ethine to 2 vols. of hydrogen, forming ethane (ethyl hydride), $C_2H_2 + 2H_2 = C_2H_6$.

Heated with an equal volume of ethene, it yields quartine, $C_2H_2 + C_2H_4 = C_4H_6$.

Oxidizing agents, such as potassium permanganate, convert ethine into *oxalic acid*, $C_2H_2O_4$, an acid formerly obtained only from plants, or by the decomposition of vegetable products.

Nitrogen, in like manner, unites directly with ethine, to form *hydrocyanic acid*. The combination is effected by passing a series of induction sparks through a mixture of equal volumes of the gases; $C_2H_2 + N_2 = 2CHN$. By bringing a small quantity of potash solution into the tube, so as to

withdraw the hydrocyanic acid as fast as it is generated, the whole of the ethine and nitrogen may be made to combine.

Ethine spontaneously inflames in contact with chlorine. If a few bubbles of chlorine are brought into a jar of the gas standing over water, a violent explosion occurs, which is attended with a bright red flash, and the separation of a large quantity of carbon. A stream of ethine, passed into chlorine, takes fire and burns with a lurid, smoky flame.

112. Coal Gas.—The gas usually employed to give light in our houses is produced by the destructive distillation of coal. Its illuminating effect is due to the hydrocarbons it contains. When coal is heated in closed vessels it is resolved into a variety of gaseous, liquid, and solid products, the relative proportion of which depends upon the temperature to which it is subjected. At a high temperature gases are mainly obtained; at a low temperature heavy tarry liquids are formed, which hold the various solid substances either in solution or in suspension. The following bodies are produced by the dry distillation of coal:—

GASEOUS.

Hydrogen,	H	Quartene,	C ₄ H ₈
Methane,	CH ₄	Ethine,	C ₂ H ₂
Carbon Monoxide,	CO	Carbon Dioxide,	CO ₂
Ethene,	C ₂ H ₄	Hydrogen Sulphide,	H ₂ S
Propene,	C ₃ H ₆	Nitrogen,	N

LIQUID.

Water,	H ₂ O	Cymene,	C ₁₀ H ₁₄
Carbon Disulphide,	CS ₂	Aniline,	C ₆ H ₅ N
Benzene,	C ₆ H ₆	Picoline,	C ₆ H ₇ N
Toluene,	C ₇ H ₈	Leucoline,	C ₉ H ₉ N
Xylene,	C ₈ H ₁₀	Phenol,	C ₆ H ₅ O
Cumene,	C ₉ H ₁₂	&c.	&c.

SOLID.

Ammonium Carbonate, NH ₄ HCO ₃	Napthalene,	C ₁₀ H ₈
Ammonium Sulphide,	Paranapthalene,	C ₁₅ H ₁₂
Ammonium Sulphite,	Chrysene,	C ₁₈ H ₁₂
Ammonium Chloride,	Anthracene,	C ₁₄ H ₁₀
Ammonium Cyanide,	Retene,	C ₁₉ H ₁₈
Paraffin,	&c.	&c.

Comparatively few of these substances are found in coal gas as actually used for illuminating purposes, the greater number being removed by the process of purification which the volatile product experiences before it is distributed. The majority of the liquid and solid substances are removed by simply cooling the volatilised matters immediately on leaving the retorts. The still gaseous portions may be subdivided under the three heads of *Illuminating Constituents*, *Diluents*, and *Impurities*.

ILLUMINATING INGREDIENTS.	DILUENTS.	IMPURITIES.
Ethene.	Hydrogen.	Hydrogen Sulphide.
Propene.	Methane.	Ammonium Sulphide.
Quartene.	Carbon Monoxide.	Ammonium Carbonate.
Ethine.		Carbon Dioxide.
Vapours of the hydrocarbon series, C_2H_{2n} , C_nH_{2n-2} and C_nH_{2n-6} .		Carbon Disulphide.
		Nitrogen.
		Oxygen.
		Aqueous Vapour.

The impurities require to be carefully removed, since they not only diminish the illuminating power of the gas, but also produce noxious compounds on burning. It is found that 1 per cent. of admixed carbon dioxide diminishes the illuminating intensity of the gas about 6 per cent. The sulphur and nitrogen compounds in coal gas are a source of much annoyance. When burnt they give rise to acid products, which rapidly corrode metal fittings, decorations, gilding of books, &c.

Fig. 76 represents the main features of the apparatus employed in the manufacture and purification of coal gas. Bituminous coal or cannel is introduced into the cylindrical or elliptical retorts *a a*, which are raised to a bright red heat. Each of the retorts is connected with an arched tube *b*, which enters midway into the long horizontal cylinder B; from this descends the tube *d*, leading to the *tar pit* *c*. The gas now traverses the series of bent iron pipes *h h h*, termed the *refrigerators*; thence it passes into the *purifier* E, and eventually finds its way into the gasometer G, when it is ready for distribution. The arched tubes *b* leading from the retorts are so arranged that they dip beneath the surface of the tar and water which condense in the horizontal pipe B. By this simple arrangement any one of the

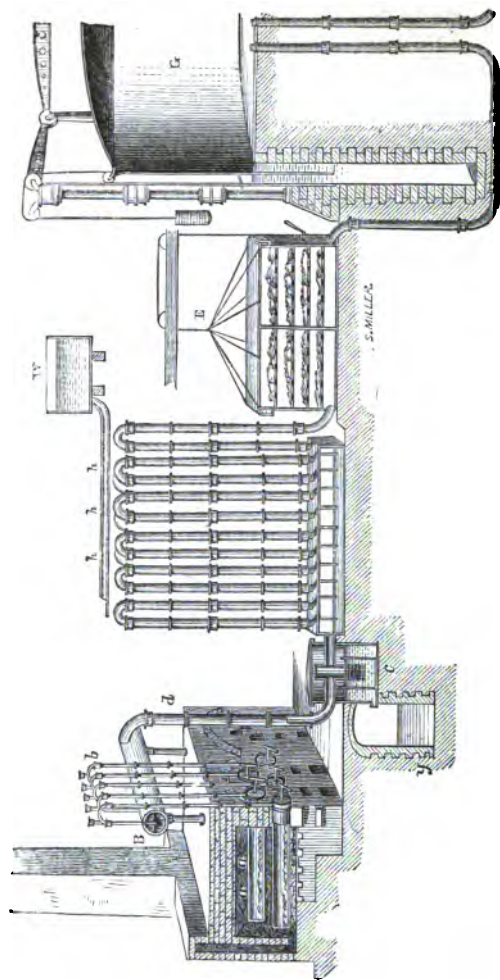


Fig. 79.

retorts can be opened without interfering with the action of the rest. The liquid in B is maintained at a constant level; as the condensed matter accumulates, it flows over through the tube *d* into the tar cistern. The greater portion of the nitrogen contained in coal is evolved as ammonia, which condenses in the aqueous vapour simultaneously formed; the ammoniacal liquor mainly collects in *c*. It is drawn off from time to time and used as a source of ammonium compounds (see p. 186). By cooling the vapours a further quantity of tar and ammoniacal liquor is obtained. The refrigerators *h h h*, in which this condensation is effected, are occasionally surrounded with cold water, which flows from the cistern W. The condensed liquor runs into the cistern *y*, and is drawn off as it accumulates. The main portion of the tar, ammoniacal compounds, and aqueous vapour is now deposited. The gas has still to be freed from sulphuretted hydrogen and carbon dioxide. It is accordingly conducted into the purifiers E, containing slaked lime or a mixture of iron oxide and sawdust, which rapidly absorb these compounds. A certain proportion of the sulphur is evolved from the retorts in the form of the highly volatile carbon bisulphide; this escapes condensation in the refrigerators, and is not absorbed in the purifiers. By properly regulating the temperature during the distillation, the amount of the carbon bisulphide may be reduced to a minimum. It is said that gas already containing the bisulphide may be purified by simply reheating it when hydrogen sulphide is formed, which may be readily absorbed by iron oxide and sawdust in the usual manner. After leaving the gasometer, the gas passes through a *governor*, by which its pressure in the mains is regulated.

The following table gives the composition of coal gas of average quality:—

Hydrogen,.....	45.58
Methane,.....	34.90
Carbon Monoxide,	6.64
Ethene,.....	4.08
Quartene,.....	2.38
Sulphuretted Hydrogen,	0.29
Nitrogen,	2.46
Carbon dioxide,.....	3.67
	<hr/>
	100.00

The value of illuminating gas is usually expressed in terms of some standard source of light. The distances at which the shadows thrown by a sperm candle burning at the rate of 7.8 grams per hour, and by the gas flame burning at the rate of 5 cubic feet per hour, are equally intense are compared. From the knowledge that the illuminating intensities vary as the squares of the distances, the value of the gas as compared with the candle is readily calculated. Thus, supposing that equally intense shadows were cast by a candle flame 4 feet distant, and by a gas flame at a distance of 15 feet, the illuminating power of the gas flame would be fourteen times that of the candle, since—

$$\frac{15^2}{4^2} = \frac{225}{16} = 14.$$

Accordingly the gas would be styled, *fourteen candle gas*.*

113. Nature and Composition of Flame.—Flame is simply gas in a state of incandescence. When a light is brought to a jet of hydrogen issuing into the air, the hydrogen combines with the oxygen with the production of great heat; the flame is the result of the heat evolved in the act of combination. We can produce this flame either by burning the hydrogen in oxygen, or the oxygen in hydrogen. This fact proves to us that the flame is merely the result of the combination of the gases. Although the oxyhydrogen flame is one of the hottest flames we can obtain, under ordinary circumstances it has a very feeble illuminating power.

The brightness or illuminating power of a flame depends (1.) on the temperature of the incandescent gases; (2.) upon their density; and (3.) on the presence of solid particles within the area of combustion. These become heated to incandescence, and act as radiant points. The illuminating effect of a flame containing solid particles is augmented by increasing the temperature.

1. The effect of temperature in increasing the luminosity

* For further information on this subject the student may consult the article, "Coal Gas," by Professor Frankland, in *Ure's Dictionary of Arts and Manufactures*.

of a flame not containing solid particles is well seen in the different appearance of the flames of sulphur and phosphorus burning in the air and in oxygen. The oxide of sulphur remains permanently gaseous; the oxide of phosphorus is only gaseous for a very short time after its production. When sulphur and phosphorus burn in the air the illuminating effect is far less than when burning in oxygen, since in the former case the temperature is lowered by the presence of nitrogen, which contributes nothing to the heat of combination, but abstracts a considerable amount of that formed by the union of the oxygen with the combustible. Under ordinary conditions phosphorus burns in chlorine with a very feeble light, but strongly heated chlorine and phosphorus vapour combine with a dazzling white flame.

2. Observation has shown that a certain relation exists between the luminosity of a flame free from solid particles and the density of its constituents; the brightest flames contain the densest vapours. Hydrogen burns in oxygen with but a feeble flame to form water; it burns in chlorine with a far brighter light, and produces hydrochloric acid, the density of which is more than twice that of water vapour. The luminosity of a flame is augmented by condensing the gaseous atmosphere which surrounds it. The combination of oxygen and hydrogen is attended with a bright light when the gases unite under great pressure. Alcohol burns with a feebly illuminating flame under ordinary conditions, but its flame becomes very bright when it is burnt under the receiver of a condensing pump. The light emitted by a burning candle at the top of a mountain is much less than that given at the bottom, although the amount of fatty matter consumed in a given time may not vary at the two spots.

3. A feebly illuminating flame increases in luminosity by projecting solid matter into it. A small quantity of finely divided charcoal blown into a hydrogen flame gives it a luminous appearance. Oxide of zinc projected into the same flame confers illuminating power upon it. On the authority of Davy it was long considered that the luminosity of a flame depended entirely on the presence within it of solid incandescent particles. The recent experiments of Frankland

have shown that this view must be modified. Arsenic burns in oxygen with a bright light, and without the immediate formation of a solid substance. A mixture of nitrogen dioxide and carbon bisulphide burns with a bright flame without the separation of solid matter. The illuminating effect of an ordinary candle or coal gas flame is, according to Frankland, due, not to the separation of solid particles of carbon, but to the formation of dense hydrocarbons, which bring about similar effects to the vapours of phosphorus and arsenic in their respective flames.

If the flame of a candle, or indeed that of any highly carbonized substance, be minutely examined, it is seen to consist of four distinct parts, as in fig. 77, which represents a candle flame.

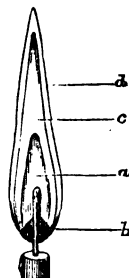


Fig. 77.

We have first a dark inner cone (*a*) immediately surrounding the wick. This is made up of the gases or vapours distilled from the wick, together with the products of their partial combustion, namely, water and the oxides of carbon: in addition, we have a considerable volume of atmospheric nitrogen. Below this is a light blue cone *b*, of comparatively small area, consisting of the combustible matter of the wick, which becomes mixed with a sufficient amount of oxygen to burn it completely. Above this is a bright, luminous cone *c*, in which the products of the distillation from the wick are still further broken up with the production of dense hydrocarbons, and possibly also with the separation of carbon. The presence of carbon in this portion of the flame is supposed to be demonstrated by the fact that a cold solid body introduced therein is immediately covered with soot. Soot, however, is not pure carbon; it contains a considerable amount of hydrogen. Moreover, the perfect transparency of this zone seems inconsistent with the presence of solid particles. Surrounding the entire flame (except at *b*) is the mantle *d*, which is feebly luminous, and of a yellowish colour; this consists of the final products of combustion of the constituents of the luminous zone mixed with atmospheric air heated to incandescence. Owing to the

luminosity, this part of the flame is not very easily seen; the readiest manner of recognizing it is to cut out a card of the shape of the flame, and hold it at such a distance from the eye as to hide the luminous zone. It may also be detected by burning a little sodium in its vicinity, when it will be coloured strongly yellow.

The following table shows the composition of a tallow candle flame at various heights above the wick (Hilgard):—

Distance from Wick.	Weight of Solids and Liquids from 1 Litre of Flame Gas.	N.	CO ₂ .	CO.	C ₂ H ₂ .	CH ₄ .	H.
9 m.m. above	0.12 grams	75.92	14.46	5.65	1.52	1.15	1.30
6 " "	0.11 "	72.28	10.90	6.25	6.04	2.68	1.85
4 " "	0.13 "	64.40	10.24	6.68	13.10	2.70	2.88
2 " "	0.38 "	59.01	10.14	7.22	17.12	3.78	2.73
0 " "	0.70 "	63.57	7.13	4.60	18.77	5.20	0.73
3 m.m. below	1.49 "	61.72	11.73	6.27	15.13	4.00	0.15

At first sight the flame of alcohol appears to be differently constituted from that of a candle; in reality, however, it has the same number of zones, although their relative areas are very different. The internal cone is very large, in consequence of the great volatility of the alcohol; the luminous portion is very small, owing, probably, to the simple manner in which the alcohol is broken up and consumed. From the feeble illuminating power of this cone the mantle appears largely developed.

The composition of the various portions of a coal gas flame has been studied by Landolt. In the following table A denotes the volume of air which has mixed with 100 vols. of coal gas to produce the flame gas at the various heights, D. $100 + A = M$ vols. of this unburnt gaseous mixture yield V vols. of flame gas. The flame employed was about 90 m.m. high. The combustion of the mixture before and after burning is as follows:—

D A M V	0 m.m.		20 m.m.		50 m.m.	
	27·08		172·76		381·66	
	27·08		272·76		481·66	
	111·41		245·96		461·23	
	M.	V.	M.	V.	M.	V.
Hydrogen,	39·30	22·66	44·00	5·49	41·37	11·95
Methane,	40·56	33·77	38·40	28·34	33·30	3·64
Carbon Monoxide,	4·95	7·34	5·73	14·05	5·56	25·14
Ethene,	4·04	4·23	4·13	4·58	5·00	2·77
Quartane,	3·15	3·06	3·14	3·29	4·34	2·68
Oxygen,	5·67	0·66	36·21	0·47	79·99	—
Nitrogen,	29·41	29·41	140·78	140·78	307·10	307·10
Carbon Dioxide, ...	—	1·96	0·37	10·11	—	32·34
Water,	—	8·34	—	38·85	—	75·61
	127·08	111·41	272·76	245·96	481·66	461·23

The *size of a flame* from gas issuing at a constant pressure is mainly dependent on the proportion of oxygen contained in the atmosphere in which it burns. The greater the quantity of oxygen the smaller is the flame. This fact is well seen by introducing a stream of oxygen into a coal gas flame burning in air; the flame will thereby be reduced considerably in size. The increased size of the flame under ordinary conditions is due to the circumstance that the air contains only one-fifth of its volume of oxygen; the combustible gas has therefore to seek, so to say, over a larger area for the oxygen required for combination.

The *colour* of a flame is modified by its temperature, and by the nature of the foreign substances introduced into it. Under ordinary conditions carbon monoxide burns with a blue flame; if heated before combustion it burns with a yellowish-red flame. When once initiated the continuation of the combination of unlimited amounts of oxygen and a combustible gas depends essentially upon this condition—that *the combining gases maintain the temperature necessary to bring about their union*. A coal gas flame may be extinguished by suddenly

introducing into it a cold copper globe. The metal so rapidly abstracts the heat from the gases that their temperature is reduced below the point at which they can combine. If a helix of thin copper wire be brought over a burning candle, the flame will immediately be extinguished. If, however, the helix and the globe be previously heated to redness, the flames will not be extinguished. This principle admits of many useful applications. Hemming's safety jet for use in the oxyhydrogen lamp is simply a tube packed with fine brass or copper wires; between the interstices of the wires the mixed gases pass, and may be inflamed at the mouth of the jet. If by chance the flame should traverse the pipe in the direction of the reservoir of mixed oxygen and hydrogen, it is immediately extinguished by the cooling action exerted by the metal, and all risk of explosion is thereby obviated. A far more important application of the same principle is seen in the safety-lamp of Sir Humphrey Davy. This is simply an ordinary oil lamp surrounded by a cylinder of wire gauze. If this lamp is introduced into an explosive atmosphere of fire-damp and air, combination occurs within the lamp, but the blue flame produced by the union of the gases is prevented from traversing the gauze, owing to the rapidity with which the burning gases are cooled down in contact with the metal. If, however, the gauze by accident becomes strongly heated, its action ceases; it allows of the transmission of the flame, and is powerless to prevent an explosion.

The well known Bunsen burner (fig. 78) partly depends for its action on this principle. It consists of a jet surmounted by a wide brass tube, at the bottom of which are several holes for the admission of air. The air and gas mix in the wide tube in such proportion that they burn at the top with a non-luminous flame.

Rarefaction of the gases prevents the continuance of combustion by retarding combination, and, consequently, the rapid development of heat. The temperature of the gases may from this cause sink below that necessary

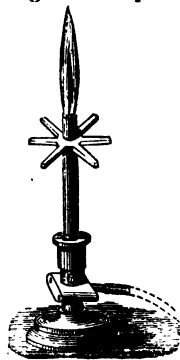


Fig. 78.

to effect union. A mixture of detonating gas (2 volumes of hydrogen and 1 of oxygen) is not explosive when rarefied to $\frac{1}{18}$ of its ordinary density. A jet of hydrogen gas will not burn when issuing into air rarefied to $\frac{1}{3}$ of its ordinary amount. By mixing oxygen with an indifferent gas like nitrogen, many phenomena of combustion are immediately arrested. If a watch spring burning brilliantly in oxygen be withdrawn into the air, rapid combustion at once ceases.

114. **The Blowpipe Flame.**—The blowpipe (fig. 79) is an instrument which serves to direct a stream of air into a candle or coal gas flame. The introduction of the air within the flame at once destroys its luminosity by effecting a more

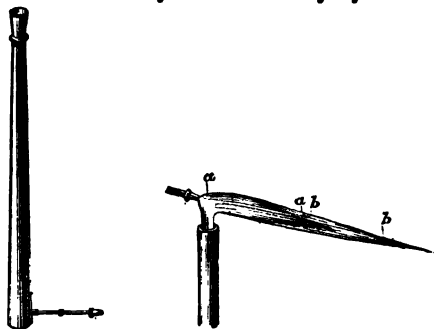
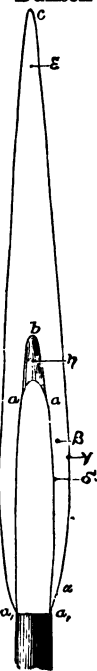


Fig. 79.

rapid combustion of the carbonaceous matter. In its character the blowpipe flame is analogous to that of the oxyhydrogen flame. Its peculiar action depends upon the possession of two distinct areas of combustion, *a a* and *b b* (fig. 79). A piece of lead glass introduced into the zone *a* is at once blackened, owing to the reduction of the lead to the metallic state; by exposing the blackened glass to the extreme point of the flame it again becomes colourless by the reoxidation of the lead. The zone *a a* is therefore termed the *reducing* flame, and that marked *b b* the *oxidizing* flame. The reducing power of the inner flame is mainly dependent on the carbon monoxide which it contains; at a high temperature this gas has great tendency to pass into the state of carbon dioxide, it is able therefore to abstract the oxygen from many

metallic oxides and salts. In the area $b b$ the carbon monoxide is completely burned, and is mixed with excess of incandescent oxygen; an oxidizable body such as metallic lead placed in this portion of the flame combines with the heated oxygen, and is converted into an oxide. The different behaviour of the two zones is of great service in analytical chemistry.

115. Bunsen Lamp Flame.—All the effects of the blow-pipe flame may be easily brought about by the aid of the flame of the Bunsen lamp. The structure of the Bunsen flame is seen in fig 80. It consists of the following parts:—(1.) *the dark cone, $a, a a a$* , consisting of cold unburnt gas mixed with about 62 per cent. of air; (2.) *the flame mantle, $a c a b$* , made up of the burning coal gas mixed with air; (3.) *luminous point, $a b a$* , only seen when the air holes at the base of the lamp are partially closed. The area of this zone may be regulated by opening or shutting the holes to a greater or less extent. The base of the flame is at a ; here its temperature is very low, the burning gas being cooled by the uprush of cold air, and by its proximity to the cold metal tube. By introducing a mixture of flame-colouring substances into this portion of the flame, it is frequently possible to obtain a succession of tints as the various bodies volatilize. Such a graduated series of colours cannot be produced in any other part of the flame; at the high temperature the whole of the substances are apt to volatilize together, without the appearance of any characteristic tints. At β is the *zone of fusion*. It is situated a little above the first third of the flame in height, and midway between the inner and outer limits of the mantle at the broadest part of the flame. At this point the flame possesses the highest temperature; it is used for testing the volatility of substances, and for determining their melting points; it is also employed for fusions at a high temperature. *The lower oxidizing flame* is situated at γ , in the outer margin of the zone of fusion; in this portion of the flame processes of limited oxidation are readily



effected. *The upper oxidizing flame* at ϵ is more particularly suited for the oxidation of comparatively large quantities of substance, and for roasting operations. It is most efficacious when the air holes are completely open. *The lower reducing flame* lies at δ , at the internal edge of the mantle, next to the dark central zone; it is especially serviceable in bringing about partial reductions. Oxides which easily part with their oxygen are here readily reduced to the metallic state. *The upper reducing flame* at η is formed by gradually closing the air holes at the bottom of the tube. The amount of carbonaceous matter within it should not be so large as to blacken a piece of porcelain held in it. It possesses stronger reducing powers than the lower *reducing zone*, owing to the absence of free oxygen in it, and to the presence of a larger quantity of unburnt carbonaceous matter. (Bunsen, *Phil. Mag.* [4] xxxii. 81).

COMPOUNDS OF CARBON AND OXYGEN.

Carbon combines with oxygen in two proportions to form—

CARBON DIOXIDE, SYMBOL CO_2 ; MOL. WEIGHT 44; DENSITY 22; and

CARBON MONOXIDE, SYMBOL CO ; MOL. WEIGHT 28; DENSITY 14.

116. Carbon Dioxide has been known for a very long time. Its main properties were described by Paracelsus and Van Helmont. Its nature, however, was more accurately investigated by Black, Priestley, and Lavoisier. It is formed synthetically by burning charcoal, or any substance containing carbon in excess of oxygen gas. It is produced by the combustion of all the ordinary kinds of fuel. It is a product of respiration, and is largely evolved from subterranean sources; it is constantly present in the atmosphere to the extent of about 4 vols. in 10,000 vols. of air.

In addition to the sources already enumerated (see p.180), carbon dioxide is largely generated in the processes of decay and putrefaction. All ordinary fermentative changes are accompanied by the formation of this gas. If a small quantity of sugar dissolved in water, and contained in a flask fitted with a cork and bent tube (fig. 81), be mixed with a little yeast, fermentation will be set up, and carbon dioxide will be

disengaged. If the end of the bent tube connected with the flask be placed in a small quantity of lime water, that liquid will soon become turbid, owing to the precipitation of calcium carbonate. By collecting, drying, and heating the calcium carbonate, the carbon dioxide may be again obtained, the lime being left behind in the *caustic* state. Immense quantities of limestone (calcium carbonate) are decomposed in this manner to form lime for building purposes. The change produced in the limestone by heat was first explained by Black.

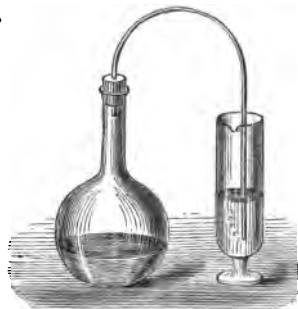


Fig. 81.

117. Its Preparation and Properties.—Carbon dioxide may readily be obtained from calcium carbonate by the action of a strong acid, such as hydrochloric acid. The apparatus seen in fig. 82 may be employed for the preparation of the gas by this method.

The form of calcium carbonate best adapted to the preparation of the gas is marble: it is broken into small pieces and introduced into the flask; the acid is poured on to it through the funnel tube. Owing to its great den-

sity (the gas is $\frac{22}{14.47} = 1.5$

times heavier than air,) it may be collected by downward displacement, as represented in the figure.

It may also be collected

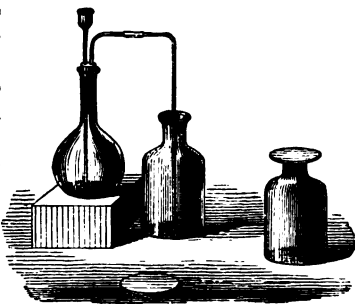


Fig. 82.

over water, but with some little loss, as it is soluble in that liquid: 100 vols. of water at 0° dissolve about 180 vols. of gas. By increasing the pressure under which the absorption is effected, the water may be made to take

up a proportionately larger quantity of the gas. On relieving the pressure, the excess of the gas over and above that which would be taken up under the atmospheric pressure escapes with effervescence. We notice this effect in the effervescing mineral waters of Vichy and Pyrmont, which are highly charged with gas at great depths, and, therefore, under great pressure. On rising to the surface the excess of gas is evolved, and gives to the water the appearance of active ebullition. The effervescence of champagne, of soda water, lemonade, &c., is due to the same cause. The carbon dioxide in these liquids usually exists under an extra pressure of from 4 to 6 atmospheres; that is to say, the solution contains from 4 to 6 times as much gas as it could ordinarily take up.

The following equation represents the decomposition of calcium carbonate by hydrochloric acid:—



Calcium carbonate, in contact with hydrochloric acid, produces carbon dioxide, water, and calcium chloride. Any strong acid which forms a soluble salt with lime, may be substituted for hydrochloric acid: the least advantageous, however, is sulphuric acid, on account of the sparing solubility of calcium sulphate. This salt, as it is formed, is deposited on the unattacked marble, and retards the further action of the acid; the elimination of the carbon dioxide, therefore, nearly ceases after a time.

Carbon dioxide is a colourless, invisible gas. It is combustible, and a non-supporter of combustion. A taper plunged into it is at once extinguished. Its inability to support combustion, and its high density, may be simultaneously shown by a variety of experiments. If the large jar (fig. 83) be filled with the gas, a thin collodion balloon, filled with air, will rebound when dropped within the jar as if from the surface of a solid; if the cork at the bottom be removed, and the gas allowed to flow upon a lighted taper placed beneath, the flame will be extinguished. The same fact may also be shown in a striking manner by allowing carbon dioxide to flow into a beaker, suspended from the arm of a balance. The apparently empty beaker

will gain considerably in weight. These properties of carbon dioxide have received an important application in the fire "extincteur." This is simply a metallic vessel, into which



Fig. 83.

carbon dioxide is compressed; by means of a stop cock, and flexible tube, a stream of the gas can be projected upon any burning material. This contrivance is particularly serviceable in checking small conflagrations.

Carbon dioxide is irrespirable; animals soon die when immersed in it, not only from the want of oxygen, but also from the direct poisonous action of the gas. Even in small quantity it produces great langour and depression; in larger quantities it occasions complete atony of the brain functions. By reason of their high density, the carbon dioxide molecules move with comparative slowness; the gas is therefore apt to accumulate at the bottom of caverns, wells, and mines. It is a common practice among well-sinkers, brewers, and others to lower a candle into the places into which they wish to descend; if the candle is extinguished the atmosphere cannot be entered with impunity, unless special precautions are taken. It is possible, however, to exist for a short time in an atmosphere in which a candle refuses to burn. It is found that a candle goes out in air when the oxygen sinks to 18·5 and the carbon dioxide rises to 2·5 per cent.

118. Ventilation.—We have already stated that carbon

dioxide is a product of combustion and of respiration. These processes are of course continually going on in our dwellings, and unless some means were present of removing the carbon dioxide produced, this gas would accumulate to such an extent as to vitiate the atmosphere. In the generality of cases the crevices of the doors and windows of an apartment are depended upon for the entrance of fresh air, and for the escape of the products of combustion and respiration; but where many persons are congregated together special means of ventilation are required. The arrangements employed in nearly all cases depend upon the fact that the temperature of the vitiated air is augmented by the vitiating process. The air expired from our lungs (which contains nearly 4 per cent. by volume of carbon dioxide) has a temperature of about 34° ; that rising from gaslights, two of which burning at the ordinary rate produce as much carbon dioxide as an adult, is of course considerably hotter. By reason of its increased temperature the contaminated air is rendered specifically lighter than the fresh and cold air, and ascends, therefore, to the ceiling of the apartment. The air near the floor of a room ordinarily well ventilated usually contains from .06

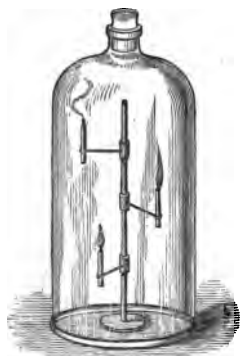


Fig. 84.

to .08 volumes of carbon dioxide per cent.; that near the roof not unfrequently contains twice these amounts. These facts are well illustrated by placing a tall stoppered jar over a number of candles attached to a support, in the manner represented in fig. 84. It will be noticed that the tapers are successively extinguished, beginning with that near the top of the bottle where the contaminated air accumulates. If the stopper be withdrawn immediately before the lowest taper is extinguished, and the jar raised a little, the flame will be revived by the entrance of fresh air and the escape of that which is vitiated. If a lighted taper is held at the bottom of the door of an apartment the flame will be blown inwards by the current of

cold fresh air; if held near the top it will be blown outwards by the escape of the warm contaminated air. The ventilation of mines is conducted on the same principles. A mine has usually two *shafts*, under one of which (the up-cast shaft) a fire is kept burning so as to create an uprush of air; cold and pure air descends through the down-cast shaft, and is made to traverse the workings, so as to sweep along with it towards the up-cast shaft the gases produced by respiration and combustion, together with those evolved from the seams. The apparatus in fig. 85 is intended

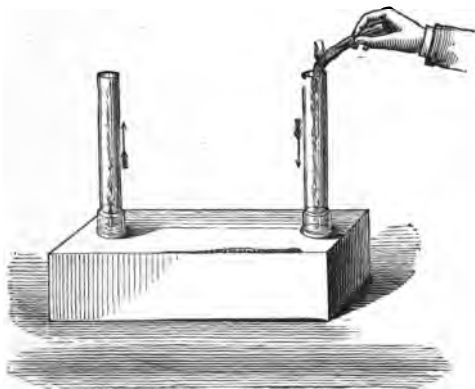


Fig. 85.

to illustrate this action. A lighted taper is placed in one of the glass chimneys; this occasions a current of air in the direction indicated by the arrows; the air stream may be rendered evident by holding a piece of smoking brown paper over the chimney corresponding to the down-cast shaft. If this chimney be closed by a cork the taper will be extinguished from the lack of fresh air. The taper may likewise be extinguished by pouring carbon dioxide down the shaft.

119. Liquid Carbon Dioxide.—Carbon dioxide may be liquefied under a pressure of 36 atmospheres at 0° , by the methods described on page 205. The liquid is exceedingly mobile, and is non-miscible with water, although readily

soluble in ether and alcohol. Its specific gravity at 0° is 0.947 (Andréeff). It boils at -78.2 , under a pressure of 760 m.m., and expands very rapidly on being heated. One vol. at 0° becomes 0.95 vols. at -10° , 1.06 vols. at $+10^{\circ}$, and 1.14 vols. at $+20^{\circ}$. Liquid carbon dioxide has feeble solvent properties. It does not redden litmus, and is a bad conductor of electricity. It is not decomposed by any ordinary reducing agents, with the exception of the alkaline metals.

120. Continuity of the Gaseous and Liquid States.—

Liquid carbon dioxide has been made the subject of a very remarkable investigation by Dr. Andrews. If the temperature of a quantity of the liquefied gas be gradually raised to about 31° , the surface of demarcation between the liquid and the gas becomes gradually fainter, and eventually disappears, and the tube seems to be filled with a perfectly homogeneous fluid. At the above temperature, termed by Andrews the "*critical point*," the carbon dioxide ceases to be liquefied under pressure. Other condensable gases and highly volatile liquids have fixed and determinate points at which they cease to be liquefied under pressure; the property is indeed common to all vaporizable liquids and condensable gases.

The critical temperature of the so-called permanent gases is so very low that we are unable to produce a degree of cold sufficiently intense, even when combined with enormous pressures, to condense them to the liquid state.

Carbon dioxide may thus be made to pass from the state of gas to that of liquid without any sudden diminution of volume occurring. If a given volume of the gas, at 50° , be exposed to gradually increasing pressure (say up to 150 atmospheres), we notice that the volume is gradually lessened with the increment of pressure, but no sudden contraction indicating liquefaction occurs. If the gas be allowed to cool down to the ordinary temperature, no breach in the continuity of the operation is observed. The carbon dioxide in the outset is a gas, and in the end becomes a liquid by a gradual transition, unaccompanied by any abrupt changes of volume. Andrews infers, from these observations, that what we style the liquid and gaseous states are simply widely separated manifestations of the same condition of matter;

there is no real line of demarcation between what we ordinarily term the various physical states. Carbon dioxide passes from the state of perfect gas to that of perfect liquid by an absolutely continuous process.

121. Solid Carbon Dioxide.—By the rapid evaporation of a portion of the liquefied carbon dioxide, the remainder may be caused to solidify. The solidified substance has such a low conductivity for heat, that it may be exposed to the air for some time without much of it evaporating. An air thermometer immersed in it sinks to -78° . Although so intensely cold, the snow-like loosely aggregated mass may be placed on the hand without evil consequence; but if pressed between the fingers, it occasions acute pain, and causes a blister like a burn. By mixing it with ether it evaporates rapidly, and produces a still greater degree of cold; by placing the mixture under the receiver of an air pump, most intense cold is produced, sufficient to liquefy, and even to solidify, the greater number of the gases. Liquid carbon dioxide itself is converted into a transparent ice-like mass when placed in the mixture.

122. Carbonic Acid.—The solution of carbon dioxide in water is supposed to form an acid—carbonic acid, H_2CO_3 —which has the same relation to the gas that nitric acid has to nitrogen pentoxide. It has been observed, when water is saturated with the gas under pressure, that more gas is evolved when the pressure is released after a few hours than after a few days. It would appear from this observation that the gas dissolves as such, but that after prolonged contact with water it becomes hydrated, and passes into the state of hydrogen carbonate, H_2CO_3 .

Carbonic acid is a very feeble acid; its solution turns blue litmus to a wine-red colour, quite different from the bright red tint produced by the mineral acids. The colour occasioned by carbonic acid is destroyed by boiling its solution, owing to the decomposition of the acid, and the dissipation of the carbon dioxide. Carbonic acid forms two series of salts possessing the general formulæ, MHCO_3 and M_2CO_3 , or $\text{M}'\text{CO}_3$, where M signifies Ag, NH_4 , or an alkaline metal, and M' , a metal like Ca, Mg Fe, &c. The

composition of a few of the principal carbonates is represented by the following formulæ:—

Sodium Carbonate (Washing Soda),.....	$\text{Na}_2\text{CO}_3 + 10 \text{H}_2\text{O}$.
Sodium Hydrogen Carbonate (Bicarbonate of Soda),.....	NaHCO_3 .
Calcium Carbonate (Limestone: Marble),...	CaCO_3 .
Ferrous Carbonate (Spathic Iron Ore),.....	FeCO_3 .
Double Magnesium and Calcium Carbonate (Dolomite),	$\text{MgCa } 2\text{CO}_3$.

Carbon dioxide passed into a solution of potassium hydroxide, is immediately absorbed with the formation of an alkaline carbonate. In contact with a solution of lime (lime water), a white precipitate of calcium carbonate is obtained. If a current of carbon dioxide be passed for some time into lime water, the white precipitate at first formed gradually disappears, and the liquid again becomes transparent—the calcium carbonate dissolving in the solution of carbonic acid. If the clear liquid be now boiled, the calcium carbonate is reprecipitated, in consequence of the destruction of the acid, and the elimination of the gas. The “temporary” hardness of spring water is due to the magnesium and calcium carbonates, held in solution by carbonic acid; the “fur” of the kettle, and the incrustation of the steam boiler, are alike caused by the precipitation of these salts on boiling the water. The precipitation may be prevented by adding sal-ammoniac to the water, whereby the earths are converted into soluble chlorides, and ammonium carbonate is produced, which volatilizes with the steam.

Although carbonic acid is a feeble acid under ordinary conditions, being expelled from its combinations even by acetic acid, it is yet capable of turning out that acid under increased pressure. A solution of calcium acetate is decomposed by carbon dioxide, under a pressure of about 28 atmospheres, with the formation of spicular crystals of calcium carbonate.

Carbon dioxide is readily absorbed from a gaseous mixture by solid potassium or sodium hydroxide. Advantage is taken of this fact in order to determine the proportion of this substance in a mixture of gases. The amount of carbon dioxide in the atmosphere may be accurately determined by agita-

ting a given volume of air with a known volume of baryta or lime water of determinate strength. The alkaline liquid absorbs the carbon dioxide, and calcium or barium carbonate is precipitated; the excess of the lime or baryta in solution is then determined by neutralizing the liquid with weak hydrochloric or oxalic acid solution of known strength. If the acid be made of such strength that 1 c.c. is equivalent to 1 mgm. of carbon dioxide, the difference in the number of cubic centimetres required for the given volume of the alkaline liquid before and after absorption at once expresses the number of milligrams of carbon dioxide in the volume of air employed.

123. The Composition of Carbon Dioxide was first demonstrated with approximate accuracy by Lavoisier by burning the diamond in a current of oxygen. He found that the gas was composed of 28 parts of carbon, and 72 parts of oxygen. More accurate experiments made on the same principle have shown that the true relation is 27.27 of carbon to 72.73

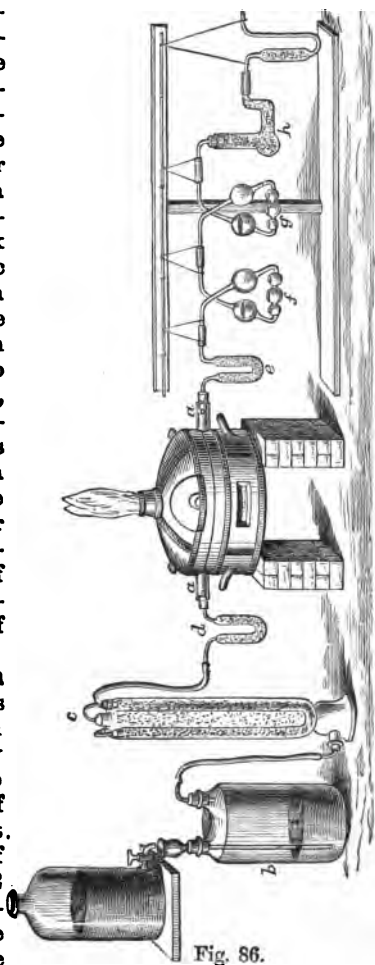


Fig. 86.

of oxygen. The determination of the atomic weight of carbon has frequently been made the subject of rigorous experiment. The exact knowledge of this weight is of great importance by reason of the great *role* played by carbon in nature, and from the fact that the proportion of the element in its compounds is almost invariably determined by weighing it in the form of carbon dioxide. The apparatus represented in fig. 86 is intended to illustrate the principle of the method employed by Dumas and Stas to determine the atomic weight of carbon. The tube *a a* passing through the furnace contains a platinum tray or boat containing a weighed quantity of diamond. It is heated to a high temperature, and a stream of oxygen from the gasometer *b*, freed from carbon dioxide and water by traversing the absorption tubes, *c d*, is passed over it. The carbon dioxide produced is completely absorbed in the weighed tubes, *e f g h*, containing potassium hydroxide both in the solid state and in solution. The decrease in weight experienced by the platinum tray gives the amount of carbon consumed, and this weight, subtracted from the gain in the absorption tube, shows the amount of oxygen with which it has united. By a series of carefully conducted experiments, in which every precaution was taken to ensure the complete oxidation of the carbon, Dumas and Stas obtained the relation above expressed—viz., 27.27 of carbon to 72.73 of oxygen. Assuming that the formula of carbon dioxide is CO_2 —i. e., that there are twice as many atoms of oxygen in the compound as of carbon—the atomic weight of carbon is found from the equation—

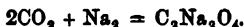
$$\frac{27.27 \times 16 \times 2}{72.73} = 12.$$

That the formula of the gas is actually CO_2 is demonstrated by its density, and by the fact that the gas contains its own volume of oxygen. If a piece of charcoal be burnt in a confined volume of oxygen, it is noticed when the combustion is at an end that the residual gas has experienced no alteration in bulk.

Carbon dioxide is slowly decomposed by a series of induction sparks into oxygen and carbon monoxide. The same decomposition is partially effected by heating it to 1200°

- 1300°. Indeed the spark produces the decomposition of the gas by the great heat which it evolves. The molecules in the proximity of the wires are intensely heated, and become *dissociated*; their recombination is prevented by their immediate diffusion into the mass of the undecomposed and cold gas.

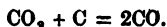
Carbon dioxide passed into melted sodium produces sodium oxalate—



This reaction constitutes a very interesting example of organic synthesis. Potassium, in contact with warm and moist carbon dioxide, produces potassium formate and acid carbonate—



124. Carbon Monoxide.—This gas is produced when carbon burns in a limited supply of oxygen. It may also be obtained by passing carbon dioxide over heated carbon—



The blue lambent flame frequently seen playing over the surface of red hot coals is formed by the combustion of carbon monoxide. The oxygen of the air entering at the bottom of the grate combines with the carbon of the coal, forming carbon dioxide, which, in contact with the ignited fuel, takes up an additional quantity of carbon, producing carbon monoxide. This gas being combustible, becomes inflamed at the top of the fire, where it again mixes with free oxygen, and burns to carbon dioxide.

Dense black coal smoke is almost invariably accompanied by carbon monoxide. Analysis A shows the composition of the gases from glowing coal; B, that of the gases accompanying dense black smoke; C, that of common brown smoke. The last two samples were from boiler fires, and were collected from the chimney (Angus Smith)—

	A.	B.	C.
Carbon Dioxide,.....	15.43	7.09	5.05
Carbon Monoxide,.....	3.49	4.46	none
Oxygen,	0.96	7.57	14.41
Nitrogen,.....	80.12	80.88	80.54
	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00

Sample B in all probability was produced by defective arrangements in the construction of the fire-places, or by negligent stoking.

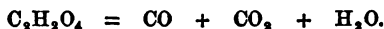
Carbon monoxide is largely evolved in many metallurgical operations, as in the smelting of iron and copper; the gas evolved from the blast furnace contains from 25 to 30 per cent., and that from the copper refining furnaces about 15 per cent., of carbon monoxide.

125. Preparation and Properties of Carbon Monoxide.

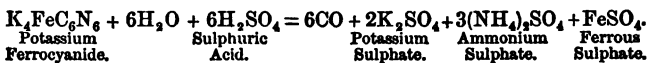
—We have already seen that warm and moist carbon dioxide in contact with an alkaline hydroxide forms a formate. By heating formic acid with strong sulphuric acid it is resolved into carbon monoxide and water—



Carbon monoxide may also be obtained from oxalic acid by heating it with sulphuric acid. The gas in this case is accompanied by an equal volume of carbon dioxide.



The mixed gases may be collected over the water trough in the ordinary way; the carbon monoxide is readily obtained free from the dioxide by agitation with potash solution. A convenient method of preparing carbon monoxide consists in heating finely powdered crystallized potassium ferrocyanide with eight or ten times its weight of strong sulphuric acid. The reaction may be thus represented—



Carbon monoxide is a colourless gas, of a density nearly equal to that of the air. It has never been liquefied, and is but sparingly soluble in water. 100 volumes of water at 15° dissolve 2.4 volumes of the gas. It burns with a beautiful

blue flame, generating carbon dioxide; the colour of the flame is somewhat modified by the temperature of the gas. The temperature of the flame is exceedingly hot; it is calculated to be over 3000°. Carbon monoxide forms an explosive mixture with oxygen. 2 volumes of the former gas mixed with 1 volume of the latter produce 2 volumes of carbon dioxide. Since 2 volumes of carbon dioxide contains 2 volumes of oxygen, it is evident 1 volume of the oxygen must have been contained in the carbon monoxide; hence this gas contains half its volume of oxygen. Two volumes of carbon monoxide weigh 28; this less 16 (the weight of 1 volume of oxygen), gives 12 for the weight of 1 carbon atom. Accordingly, the formula of the gas is CO.

Bunsen has accurately investigated the phenomenon of the combination of oxygen and carbon monoxide as effected by the induction spark. When the two gases are mixed in the proportion of 2 volumes of carbon monoxide and 1 volume of oxygen, and the mixture is inflamed, it does not wholly and instantly burn to carbon dioxide as we should *a priori* expect. In the outset, only one-third of the carbon monoxide forms carbon dioxide, whereby the temperature of the mass is raised from 0° to 3033°; by radiation and conduction the temperature becomes lowered to 2558°, after which combustion recommences, and continues until half the carbon monoxide is consumed. The combustion is again suspended until the temperature sinks to about 1146°, when a third phase of combustion is set up, followed by a period of inaction, these alternate phases of constant and decreasing temperature being repeated until the gas is completely burnt. Bunsen has also determined the velocity of propagation in the combustion of the mixture, and he finds it to be less than 1 metre per second.

126. Action on the Economy.—Carbon monoxide is an excessively poisonous gas. It acts rapidly on the blood, combining with the hæmoglobin to form *carboxy-hæmoglobin*, a body possessed of a bright red colour. The poisonous action of the gas appears to be due to the derangement of the functions of the blood in consequence of the creation of this compound, which possesses a certain degree of stability, and is less easily decomposed than oxyhæmoglobin (see p. 75).

Carbon monoxide is always produced in more or less quantity by burning charcoal and coke. The fatal effects which occasionally follow the combustion of these substances in ill ventilated apartments are due to the presence of this gas.

COMPOUNDS OF CARBON AND NITROGEN.

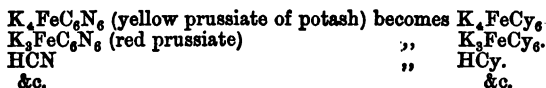
127. Cyanogen.—Carbon and nitrogen cannot be made to combine directly, but if a stream of nitrogen gas be passed over a strongly heated mixture of charcoal or carbonaceous matter and an alkali such as potash, an *alkaline cyanide* is produced. The formation of *potassium cyanide*, KCN, is occasionally seen in the blast furnace of the iron smelter, from the action of the nitrogen of the air upon the carbon of the coke, and the alkali contained in the clay or limestone. This reaction has been proposed as a method of utilizing the nitrogen in the air. If baryta be substituted for potash, and the mixture heated in air, barium cyanide is formed, which, on treatment with superheated steam, yields *ammonia* and barium carbonate. Ammonium cyanide is said to be produced by the combustion of coal gas which has passed through aqueous ammonia. Compounds containing cyanogen are prepared on the large scale by heating a mixture of nitrogenous organic matter, such as hides, hoofs, feathers, &c., with potassium carbonate and scrap iron. On lixiviating the mass with water, and recrystallizing the soluble portion, potassium ferrocyanide, or yellow prussiate of potash ($K_4FeC_6N_6 + 3H_2O$) is obtained. From this salt, and from potassium cyanide, the remaining compounds of cyanogen are directly or indirectly prepared.

Many of the compounds of cyanogen possess a very striking relation to those of chlorine. The nature of this relationship is apparent from the following formulæ—



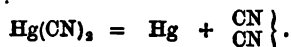
These bodies are produced by analogous reactions. Thus, HCN (hydrocyanic acid) is obtained by heating potassium cyanide with sulphuric acid, exactly in the same manner that HCl (hydrochloric acid) is prepared from potassium chloride. Potassium cyanide and chloride are isomorphous—i. e., they

possess the same crystalline shape. Silver cyanide and chloride are both white, insoluble compounds, obtained by mixing a soluble salt of silver with a soluble chloride or cyanide. It is evident therefore from the above formulæ that the group CN behaves as an element—for example, like chlorine—going in and out of combination like a simple substance. Such a group of elements is called a **compound radical**, and to indicate the fact that the group CN behaves like a simple substance, it is frequently represented by the contracted symbol Cy. Thus—

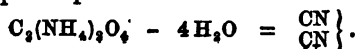


Instances of compound radicals are far more frequent in organic than in inorganic chemistry; indeed, it was at one time proposed to define organic chemistry as the *chemistry of the compound radicals*, a definition intended to indicate a supposed difference in the constitution of organic and inorganic derivatives.

128. Preparation and Properties of Cyanogen.—Cyanogen, $\left. \begin{matrix} CN \\ CN \end{matrix} \right\}$, was discovered by Gay Lussac in 1815, and is interesting as being the first compound radical which was isolated. It may be readily obtained by heating silver or mercuric cyanide, or a mixture of mercuric chloride and potassium cyanide—



In reality, however, the decomposition is not quite so simple as the above equation would indicate: a portion of the cyanogen becomes converted into a brown infusible substance, termed **paracyanogen**. The formation of this body depends upon the temperature and pressure at which the mercuric cyanide is heated. Another interesting mode of formation consists in dehydrating ammonium oxalate by means of phosphoric pentoxide—



Cyanogen is a colourless gas of a remarkable odour. It cannot be economically collected over water, as it dissolves in that liquid; 1 vol. of water absorbing about 4.5 vols. of the gas. The aqueous solution is readily decomposed; the cyanogen being transformed into ammonium oxalate, urea ($\text{CH}_4\text{N}_2\text{O}$), and a substance called azulmic acid ($\text{C}_2\text{N}_2\text{H}_2\text{O}$). As cyanogen (unlike chlorine) does not attack mercury, it may be collected over that metal.

Cyanogen burns in the air with a purple flame, forming carbon dioxide and nitrogen, $\text{C}_2\text{N}_2 + \text{O}_4 = \text{CO}_2 + \text{N}_2$. The same decomposition is effected by exploding it with oxygen. Cyanogen is one of the most easily liquefiable of the gases. By simply cooling it down to -20° , or by exposing it to a pressure of 4.5 atmospheres at the ordinary temperature of the air, it condenses to a colourless, highly refractive liquid of sp. gr. 0.86; by strongly cooling the liquid, it solidifies to a crystalline, ice-like mass, melting at -34° . Cyanogen may readily be transformed into compounds usually regarded as organic by the action of purely inorganic bodies. When treated with a strong aqueous solution of hydrochloric acid, it yields *oxamide*, $\text{C}_2\text{N}_2\text{H}_4\text{O}_2$; by nascent hydrogen, evolved from tin and hydrochloric acid, it is converted into *ethene diamene*, $\text{N}_2(\text{C}_2\text{H}_4)\text{H}_4$.

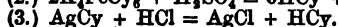
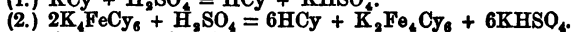
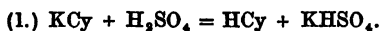
129. Paracyanogen, C_xN_x .—This body may be regarded as an allotropic modification of a compound radical. It stands in exactly the same relation to ordinary cyanogen that ozone stands to oxygen. It is merely condensed cyanogen. The degree of condensation in the paracyanogen is unknown.

By simply heating this substance to a high temperature, in a vacuum or in an atmosphere incapable of acting chemically upon it, as in nitrogen, it is reconverted into cyanogen. Paracyanogen may be obtained in quantity by heating mercuric cyanide in small portions, in sealed tubes, to about 440° (in the vapour of boiling sulphur). Nearly one-half of the cyanogen is thus transformed into the polymeric modification. By opening the tubes, and heating the mass to 440° in a current of cyanogen gas, it may be completely freed from mercury.

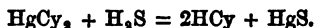
Troost and Hautefeuille have determined the relation

which exists between the temperature and pressure and the formation of paracyanogen. When silver cyanide is heated to 440° in a vacuum, only 17 per cent. of the cyanogen is converted into paracyanogen, and only 20 per cent. under the ordinary pressure of the atmosphere; but, if the salt is heated in sealed tubes under a pressure of 60 atmospheres, 64 per cent. of the cyanogen is transformed into paracyanogen. If the silver cyanide be heated to 600° in sealed tubes, when the pressure amounts to 80 atmospheres, 76 per cent. of paracyanogen is obtained. On the other hand, if the paracyanogen be heated to 860° , it is completely reconverted into cyanogen.

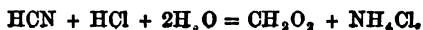
130. Hydrocyanic Acid (*Cyanide of Hydrogen, Formonitrile, Prussic Acid*) HCN or HCy .—We have already stated that this body may be formed synthetically by passing a series of induction sparks through a mixture of nitrogen and ethine (p. 225). It may more readily be obtained from the metallic cyanides—(1.) By the action of sulphuric acid upon potassium cyanide; or (2.) Upon potassium ferrocyanide; or (3.) By agitating silver cyanide with dilute hydrochloric acid:



The anhydrous acid is most readily obtained by passing a stream of sulphuretted hydrogen over gently heated mercuric cyanide—



The gas must be condensed in a freezing mixture as it boils at 26.5° . The anhydrous acid has a sp. gr. of 0.7 at ordinary temperatures. If the liquefied acid be allowed to volatilize rapidly, the unevaporated portion solidifies. The vapour of hydrocyanic acid burns in the air, and explodes when mixed with oxygen, forming carbon dioxide, water, and nitrogen. When heated with potassium, hydrogen is eliminated, and potassium cyanide is formed. The liquefied acid is suddenly decomposed when warmed with hydrochloric acid solution, forming ammonium chloride and formic acid—



If, however, the vapours of the dry acids be mixed at a low temperature, *methenylammonium chloride* $\left. \begin{array}{c} \text{CH}' \\ \text{H} \end{array} \right\} \text{NCl}$ is obtained as a white, crystalline, odourless substance, which gradually decomposes in contact with air, and quickly when dissolved in water forming ammonium chloride and formic acid.

The fixed alkalies at a high temperature produce a similar decomposition, the acid being resolved into ammonia and formic acid. Cyanide of hydrogen dissolves in water in all proportions; its solution is lighter than water, and slightly reddens litmus. The strong acid is intensely poisonous, one drop of it being sufficient to cause instant death. Its vapour is also excessively poisonous, and even when largely mixed with air it produces giddiness and headache, accompanied by a peculiar irritation of the fauces. The dilute acid of the Pharmacopœia contains about 2 per cent. of HCN. The solution, however, is liable to change on account of the great volatility of the substance, and by reason of its tendency to decompose into ammonium formate and other products. The aqueous acid is more stable in proportion to its degree of dilution. The presence of hydrochloric acid in slight quantity tends to prevent change. The addition of an alkali, however, promotes the decomposition. Hydrocyanic acid is immediately converted into ammonia, and potassium cyanide and formate on treatment with potassium hydroxide—



Hydrocyanic acid exists in the juices of many plants, or is formed by the immersion of parts of the plants in water. The acid is produced from the kernels of bitter almonds, plums, cherries, apricots, the blossoms of the sloe and mountain ash, and the leaves of the peach, cherry-laurel, &c. The greater portion of the acid obtained does not exist preformed in the plants; it is derived from a substance called *amygdalin*, which under the influence of a ferment termed *emulsin* is converted into *glucose*, *bitter almond oil*, and *hydrocyanic acid*.

Hydrocyanic acid may be readily detected (1.) by its peculiar odour, and (2.) by reactions with the oxides of iron,

and with ammonium sulphide. The liquid containing the hydrocyanic acid is made alkaline with caustic potash, and is then mixed with ferrous sulphate solution containing a slight quantity of ferric chloride; on adding hydrochloric acid to dissolve the precipitated oxides of iron, prussian blue is obtained. If the liquid suspected to contain hydrocyanic acid be mixed with ammonium sulphide and evaporated to dryness, ammonium sulphocyanate is obtained, which on the addition of a drop of ferric chloride solution gives an intense blood-red coloration of the sulphocyanate of iron.

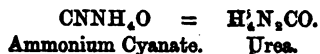
131. The Cyanides.—Hydrocyanic acid is monobasic. The cyanides are an important class of salts. Many of them are of exceedingly complicated constitution, from their tendency to unite with one another to form double cyanides. The following formulæ give the composition of the more important cyanides:—

KCy,	Potassium Cyanide.
AgCy,	Silver Cyanide.
AgCy.KCy,	Double Cyanide of Silver and Potassium.
AuCy.KCy,	Double Cyanide of Gold and Potassium.
NiCy.2KCy,	Double Cyanide of Nickel and Potassium.
Co ₂ Cy ₆ .6KCy,	Potassium Cobalticyanide.
Fe ₂ Cy ₆ .6KCy,	Potassium Ferricyanide.
CoCy ₄ .4KCy,	Potassium Cobaltocyanide.
FeCy ₄ .4KCy,	Potassium Ferrocyanide.

Cyanides may be detected by fusing them with sodium thiosulphate (hyposulphite), whereby they are converted into sodium sulphocyanate, which gives a red coloration with ferric chloride. A crystal of the thiosulphate is fused in the loop of a platinum wire with a minute quantity of the substance to be examined until sulphur begins to volatilize; the fused mass is then placed in a few drops of ferric chloride, which is immediately reddened if any alkaline sulphocyanate has been formed.

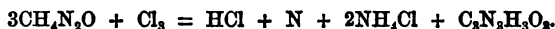
132. Cyanic Acid, CNHO or CyHO.—This substance is produced by heating its polymer *cyanuric acid*, $C_3H_3O_3$, or by heating urea with phosphoric pentoxide. In combination with potassium it may be easily obtained by heating dry potassium ferrocyanide with manganese dioxide or red lead. If the potassium cyanate so obtained be decomposed with ammonium sulphate, and the solution of ammonium cyanate

be concentrated, *urea* crystallizes out, and may be purified by recrystallization from alcohol—



This transformation, which was first observed by Wöhler in 1828, is of interest as constituting one of the earliest discovered cases of the formation of a substance formerly only to be obtained by the vital processes of animals. Cyanic acid is a thin, colourless liquid of sp. gr. 1.14 at 0°; it possesses a very pungent odour, and rapidly attacks the skin, producing severe pain. It readily changes, ~~when~~ when in a freezing mixture, into *cyamelide*, a snow-white substance resembling porcelain. At the ordinary temperature of the air the transformation is complete in a few minutes, and with the development of so much heat that the substance explodes. When mixed with water the free acid is gradually resolved into carbon dioxide and ammonia. Cyanic acid is monobasic, and gives rise to a series of salts, many of which may be obtained in well defined crystals. The cyanates are distinguished from the cyanides by the formation of a greenish-brown precipitate with copper nitrate, and by the non-formation of a precipitate with the chlorides of tin and iron.

133. **Cyanuric Acid**, $\text{C}_3\text{H}_3\text{O}_3$, bears the same relation to cyanic acid that para-cyanogen bears to cyanogen. If urea be heated with chlorine, it swells up, and is resolved into hydrochloric acid, nitrogen, ammonium chloride, and cyanuric acid—



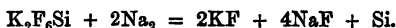
Cyanuric acid is slightly soluble in water, from which it separates in large colourless efflorescent crystals, containing 2 atoms of water of crystallization. It is a feeble acid, and is not poisonous. It is tribasic, and forms two series of crystallizable salts, termed cyanurates, normal and acid, and which are distinguished from the cyanates by their sparing solubility in water.

134. **Cyamelide** $n(\text{CyHO})$ is the white inodorous substance formed in the transformation of cyanic acid. On heating it is reconverted into this acid, but on treatment

with potash solution it yields potassium cyanurate. When its solution in strong sulphuric acid is heated, it is converted with evolution of carbon dioxide into cyanuric acid.

135. Silicon—Symbol Si; atomic weight 28.—Silicon, although the most abundant of the solid elements, is never found free in nature. It exists in combination with oxygen as silicon dioxide or silica, SiO_2 , a substance which occurs crystallized as quartz or as a crystal, and non-crystalline in the form of flint, chalcedony, opal, &c. Silicon dioxide enters largely into the composition of many minerals, such as felspar, which is the main constituent of primitive rocks. The clays are essentially silicates of alumina. Silica is found also in the vegetable kingdom; the ashes of wheat, of grass, &c., contain comparatively large quantities of this substance; the rigidity of the stems of the cereals is mainly due to silica.

Silicon is most readily obtained by heating silicofluoride of potassium with sodium—

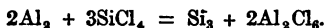


On treating the deflagrated mass with water the fluorides are dissolved, and silicon is left as a dark brown amorphous powder. It may also be prepared by heating metallic sodium in the vapour of silicon tetrachloride. It is oxidized by a hot solution of potash, and by nitro-hydrochloric or hydrofluoric acids. When heated in the air it burns, and is converted into the dioxide; it also suffers oxidation when heated with nitre or potassium chlorate. If strongly ignited in a covered crucible it becomes denser, and is less prone to oxidation; in this state it may even be heated in the oxyhydrogen flame, or fused with nitre, without alteration.

Silicon may be obtained in hexagonal crystals, resembling graphite, by fusing aluminium with silicofluoride of potassium, or by heating a mixture of aluminium, cryolite (Na_3AlF_6), and powdered glass free from lead. On treating the metallic button, first with hydrochloric and then with hydrofluoric acid, silicon is left in hexagonal tables of sp. gr. 2.49. Graphitic silicon conducts electricity, and resists the action of most acids. It is converted into the tetrachloride on heat.

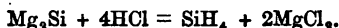
ing in a stream of chlorine, and into *silicic chloroform*, SiHCl_3 , when heated in hydrochloric acid gas.

Silicon may also be prepared in the form of iridescent dark-red hexagonal prisms by heating aluminium in the vapour of silicon tetrachloride. A portion of the aluminium is converted into aluminium chloride, which sublimes, and the eliminated silicon gradually saturates the remainder of the metal, and crystallizes out—



A more economical method of preparing crystalline silicon consists in fusing a mixture of silicofluoride of sodium with sodium and zinc. The mass is allowed to cool when the silicon assumes the form of long needles. The greater portion of the zinc may be removed by simply reheating the mixture, when the metal fuses. The crystals of silicon may be freed from the last traces of zinc by digestion with hydrochloric and nitric acids. By strongly heating the metallic mass the zinc may be volatilized; the silicon is thus obtained fused, and it may be cast into bars.

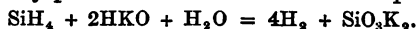
136. **Silicon Hydride**, SiH_4 , corresponding to marsh gas, may be obtained by dissolving magnesium silicide in hydrochloric acid—



Magnesium silicide is prepared by heating a mixture of 4 parts fused magnesium chloride, 3.5 parts silicofluoride of sodium, and 1 part fused common salt, with 2 parts of sodium in small fragments. On treating the mass with hydrochloric acid, silicon hydride is evolved, mixed with free hydrogen. The mixture takes fire spontaneously in air, forming a white fume of silica; if the supply of air is limited, amorphous silicon is deposited. The gas may be obtained unmixed with hydrogen by the decomposition of *triethylic silicoformate*—



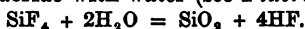
When perfectly pure it is not spontaneously inflammable in the cold, but when gently heated it bursts into flame. It is decomposed by potash in accordance with the equation—



If the gas be led into solutions of copper sulphate or silver

nitrate, silicides of these metals are precipitated. These compounds are easily decomposed, and suffer oxidation on exposure to air.

137. **Silicon Dioxide, or Silica** (SiO_2), occurs native in fine large crystals and nearly pure, in the form of quartz or rock crystal; the amethyst is a purple modification of quartz; the cairngorm is yellow or brown quartz. Hornstone, jasper, flint, opal, &c., are modifications of silica. Silicon dioxide may be obtained by burning silicon in air or oxygen, or by decomposing silicon fluoride with water (see *Fluorine*)—



Silicon dioxide enters into the composition of many minerals—*e. g.*, feldspar, andalusite, leucite, analcime, &c. The silica may be isolated by fusing the minerals with sodium carbonate, digesting the fused mass with hydrochloric acid, evaporating to complete dryness, and washing the insoluble residue with hot water, when the pure amorphous oxide remains as a soft white powder. This process is frequently used in the analysis of silicates. The silica so obtained is insoluble in water, and in all acids with the exception of hydrofluoric acid. It has a sp. gr. of about 2.2; the crystalline variety (quartz) is somewhat denser, its sp. gr. being about 2.7. It is worthy of note, however, that a naturally occurring crystalline modification, discovered by G. vom-Rath, and termed by him *tridymite*, has a sp. gr. of only 2.3. The crystalline form of tridymite is perfectly dissimilar from that of quartz. Silica fuses, at a very high temperature, to a clear transparent glass. It cannot be vaporized under ordinary conditions, but, if strongly heated in a rapid current of steam, it appears to volatilize slightly; nodules of this apparently sublimed silica are occasionally met with in the blast furnaces. Silica, more especially the amorphous variety, is readily dissolved by hot solutions of the alkaline hydroxides. It is also soluble to a slight extent in solutions of the alkaline carbonates. By reason of the solvent action of these substances, silica is found in nearly all natural waters. The hot springs rising in the neighbourhood of volcanoes are frequently saturated with silica; as the water becomes cooled this substance is deposited, and forms an incrustation round the mouth of the

spring. A remarkable example of such a super-saturated solution of silica is afforded in the geysers of Iceland.

138. **Silicic Acid**, analogous to carbonic acid, was obtained by Graham, by adding a solution of an alkaline silicate to hydrochloric acid, and pouring the mixture to a depth of about half an inch on to a *dialyser*, made by stretching a sheet of parchment paper between two hoops of wood or gutta percha (fig. 87). The dialyser is floated upon water;

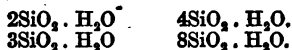


Fig. 87.

the sodium chloride and excess of hydrochloric acid pass through the paper; and, if the water be occasionally changed, pure silicic acid is left in the dialyser. Silicic acid has, therefore, a very low power of diffusion; it belongs to the class of substances termed *colloids* by Graham, in contradistinction to those substances which pass readily through membranes, and which are termed *crystalloids*. The inequality in the rates at which different substances pass through moistened membranes may occasionally be taken advantage of to effect their separation. If a mixture of potassium and sodium chlorides in solution is poured upon the dialyser floating upon water, it will be found that a considerable quantity of the potassium salt will make its way through the membrane before any appreciable amount of sodium chloride can be observed in the outer liquid. This process of *dialysis* is occasionally made use of in toxicological research. If a liquid containing a large quantity of colloidal organic matter (*e. g.*, the contents of a stomach), and suspected to contain arsenious trioxide or strychnine, be poured on to the dialyser, the oxide or the alkaloid will pass through the membrane, and may readily be detected in the water.

The solution of silicic acid obtained by dialysis may be concentrated by boiling it down in a flask till it contains about 14 per cent. of silica. It forms a tasteless and limpid liquid of a feeble acid reaction. It is gradually converted into a clear transparent jelly, which shrinks considerably on drying; it may be preserved for a longer time by the addition of a minute quantity of hydrochloric acid, or by a solution of

potash or soda. A small quantity of sodium carbonate brings about its coagulation in a few minutes. When evaporated *in vacuo* it leaves a clear transparent mass of the composition H_2SiO_3 . The following series of hydrates of silica have been obtained by Merz—



These substances are very unstable; the first members readily part with a portion of their water on exposure to air, and the others are very hygroscopic.

The mineral silicates are very abundant. The following formulæ exhibit the composition of some of the more important members:—

Olivine,	$\text{Mg}_2\text{O}_3\text{SiO}_2$.
Serpentine,	$\text{Mg}_3\text{O}_4\text{Si}_2\text{O}_5 + 2\text{H}_2\text{O}$.
Kaolin,	$\text{Al}_2\text{O}_3\text{Si}_2\text{O}_5 + 2\text{H}_2\text{O}$.
Augite,	MgOSiO_3 .
Felspar,	$\text{K}_2\text{Al}_2\text{O}_6\text{Si}_2\text{O}_{11}$.

These substances occur naturally as distinct crystalline compounds, and when intimately mixed form the more commonly occurring rocks. Granite is a mixture of mica, quartz, and felspar; porphyry and trachyte are composed mainly of felspar, basalt of felspar, and augite; trap rock is composed of an intimate mixture of hornblende (MgOSiO_2) and felspar; and serpentine rock is mainly made up of serpentine.

139. Leukone or Silico-formic Acid, SiH_2O_2 , is obtained by the action of water on silicon chloroform, or by exposing chryseone to light (*vide infra*). It is a white, bulky powder, lighter than water; it may be heated to 300° without change, but at a higher temperature it gives off hydrogen and silicon hydride. It is slightly soluble in water, and is immediately decomposed by caustic alkalis with evolution of hydrogen. It is a powerful reducing agent, separating metallic gold from its solution, and giving a black precipitate of silver silicate with ammoniacal silver nitrate solution.

140. Chryseone ($\text{Si}_4\text{H}_4\text{O}_3$?) is an orange-coloured substance obtained by digesting calcium silicide with strong hydrochloric acid. It is insoluble in water, alcohol, and indeed in nearly all solvents. When exposed to sunshine it quickly

becomes lighter in colour, gives off hydrogen, and is converted into leukone. The hydroxides convert it into silica, with evolution of hydrogen. In presence of alkalies it rapidly reduces solutions of copper, lead, gold, silver, palladium, &c. A compound of the formula $\text{Si}_4\text{H}_8\text{O}_6$ is produced by treating calcium silicide with dilute hydrochloric acid. It forms colourless laminæ, which, when dry, inflame spontaneously in air, leaving a mixture of silicon and silicon dioxide.

141. Silicon Nitride is formed by heating silicon to a high temperature in a stream of nitrogen. It is a white, infusible mass, which may be ignited in air without oxidation. It is dissolved only by hydrofluoric acid, with which it forms ammonium silicofluoride. Heated in a stream of moist carbon dioxide it forms ammonium carbonate; and when fused with potassium carbonate it yields silicate, cyanide, and cyanate of potassium. Its composition is not definitely established.

No carbide of silicon is known.

CHAPTER X.

THE HALOGENS.

THIS term is applied to a well characterized group or *family* of elements, the members of which, four in number, are named chlorine, bromine, iodine, and fluorine. Among the first three especially exist relations of a very intimate nature; thus, each combines with one atom of hydrogen to form an acid, termed respectively hydrochloric, hydrobromic, and hydriodic acid. Fluorine also combines with an atom of hydrogen to form hydrofluoric acid. The hydrogen in each acid is replaceable by an equivalent amount of potassium or sodium to form salts which are analogous in physical properties to sea-salt, whence the name *halogen* applied to the group, from *ἅλς*, *ἅλς*, *sea-salt*, and *γεννάω*, *to produce*. The physical characters and properties of the three elements

exhibit a remarkable gradational difference; thus, at ordinary temperatures chlorine is a gas, bromine a liquid, and iodine a solid. Equal bulks of the three substances, when in the state of true gas, show a similar gradation in their weights, the weight of the bromine vapour being the mean of that of the chlorine and iodine—

Cl,	35.5	} 80.7 mean.
Br,	80	
I,	126.8	

In chemical activity also bromine is midway between chlorine and iodine; thus, bromine eliminates iodine from hydriodic acid, whilst chlorine eliminates bromine from hydrobromic acid.

142. Chlorine.—Symbol Cl; atomic weight 35.5; density 35.5.

This substance was discovered by Scheele in 1774, and termed *oxymuriatic acid* by Berthollet, on the supposition that it contained oxygen. Its elementary nature was established in 1810 by Davy, who proposed the name by which the body is now called. Chlorine is never found free in nature; it exists in large quantity in combination with sodium, potassium, calcium, magnesium, &c. Immense deposits of alkaline chlorides are found in Galicia, Tyrol, Transylvania, Spain, and in England (particularly in Cheshire). Sea water also contains chlorides in large quantity; by far the main portion of the soluble matter consists of sodium chloride (see p. 141). Many mineral springs also contain common salt; some of them are so rich in this constituent that they are utilized as sources of it.

Chlorine may readily be obtained from its combination with sodium by gently heating a mixture of common salt, manganese dioxide, and sulphuric acid—

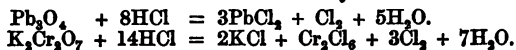


The gas may also be prepared by the action of hydrochloric acid upon manganese dioxide, with the simultaneous formation of manganous chloride and water—

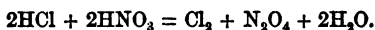


Both these processes are largely used in chemical manufactories in the preparation of the chlorine for bleaching powder,

potassium chlorate, &c. Many other peroxides, and certain oxisalts, may be substituted for manganese dioxide in the above equation; thus, red lead and acid potassium chromate generate chlorine when heated with hydrochloric acid—



If the heated vapours of nitric and hydrochloric acids be allowed to react upon another, chlorine, nitrogen tetroxide, and water are produced. By passing the products through strong sulphuric acid, the last two substances are retained, the chlorine being unabsorbed—



This process has been proposed for use in alkali works in which bleaching powder is made. A mixture of Chili salt-petre and common salt is heated with sulphuric acid, and the mixed products are treated with strong sulphuric acid. The chlorine is converted into bleaching powder, the nitrogen vapours are used in the manufacture of sulphuric acid, and the residual sodium sulphate is converted into sodium carbonate.

Chlorine is a yellowish-green gas (whence its name, from *χλωρος*), of a pungent and irritating odour; it cannot be respired, as it rapidly attacks the membranes. Water dissolves about twice its volume of chlorine, and the solution possesses the characteristic odour and colour of the gas. On cooling a saturated solution of chlorine in water to 0° , a solid crystalline hydrate, having the composition $\text{Cl}_2 \cdot 10\text{H}_2\text{O}$, separates out. On account of the solubility of the gas in water, it cannot be collected over the trough in the ordinary manner. As it is 35.5 times heavier than hydrogen (and therefore $\frac{35.5}{14.47} = 2.4$ times heavier than air), it may readily be collected by downward displacement in the manner seen in fig. 88. Chlorine cannot be collected over mercury, as it rapidly attacks that metal.

Chlorine is a very potent chemical agent, combining with many substances, even at the ordinary temperature. Phosphorus spontaneously ignites in the gas, forming phosphoric trichloride, which, in contact with excess of chlorine, is ulti-

mately converted into phosphoric pentachloride. Arsenic and antimony, when pulverized, and copper, tin, lead, and iron, when finely divided, burn in chlorine, to form chlorides. Many



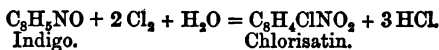
Fig. 88.

compounds unite directly, and at the ordinary temperature, with chlorine—*e. g.*, sulphur dioxide, ethene, and carbon monoxide. Chlorine rapidly attacks many organic substances, forming *addition products*, as in the case of ethene (see p. 220); or *substitution products*, as in the case of methane (see p. 218). The gas, indeed, has an intense affinity for hydrogen; a lighted taper, plunged into an atmosphere of chlorine, continues to burn with a dull lurid flame, accompanied by much soot, the chlorine preferring to unite with the hydrogen to the exclusion of the carbon. For the same reason, the non-luminous flames of the Bunsen lamp and of alcohol become smoky when burnt in chlorine. If a piece of paper, moistened with oil of turpentine, $C_{10}H_{16}$, be thrust into a jar of the gas, it takes flame, and burns with a cloud of smoke.

By reason of its tendency to unite with hydrogen, chlorine acts indirectly as an oxidizing agent in presence of moisture. Many metallic protoxides are converted into peroxides by the action of the gas in presence of water, the hydrogen of which combines with the chlorine to form hydrochloric acid,

whilst the liberated oxygen attacks the metallic oxide. If a stream of chlorine be led into an alkaline solution containing sulphur, or a sulphur compound in solution or suspension, the sulphur, in presence of water, is rapidly oxidized by the nascent oxygen to the state of sulphuric acid. The oxidizing action of chlorine is frequently made use of in chemical analysis.

Chlorine destroys many organic colouring matters; its bleaching action is due to its power of liberating oxygen. If chlorine or an aqueous solution of the gas be allowed to act upon indigo, the blue colour is quickly discharged; a portion of the chlorine combines with hydrogen to form hydrochloric acid, whilst another quantity displaces hydrogen in the indigo to form the slightly coloured *chlorisatin*.—



Chlorine is occasionally used as a deodorizing agent, and as a disinfectant; its action depends upon its power of attacking organic substances by eliminating hydrogen, or by indirectly bringing about their oxidation.

Chlorine may be condensed by subjecting it to a pressure of about $8\frac{1}{2}$ atmospheres at the ordinary temperature, and of 6 atmospheres at 0° , to a yellow mobile liquid of sp. gr. 1.33, which, according to Regnault, boils at -33.6° . Its liquefaction may be readily effected by sealing up a quantity of the chlorine hydrate in a bent tube, and gently heating it; the hydrate melts, and the condensation of the chlorine is brought about by its own pressure. Although chlorine is so readily condensed to a liquid, it has hitherto resisted all attempts to effect its solidification.

143. Hydrochloric Acid (*Chloride of Hydrogen, Chlorhydric Acid, Muriatic Acid, Spirit of Salt*)—Symbol HCl; molecular weight 36.5; density 18.25.—This substance constitutes the only known compound of chlorine and hydrogen. It occurs to a slight extent in nature, being found in the exhalations from active volcanoes. It may be synthetically obtained by mixing equal volumes of chlorine and hydrogen, and exposing the mixture to the action of diffuse daylight. The chlorous colour of the mixture gradually disappears,

and on opening the vessel the gas is found to have lost the odour of chlorine, and to have acquired the property of fuming strongly in the air; one volume of chlorine and one volume of hydrogen have combined together to form two volumes of hydrochloric acid gas. If the two gases, both perfectly pure, and mixed in equal bulks, are exposed to direct sunlight, they combine with explosion; an explosive combination may also be effected by the electric light, or by the flame of burning magnesium, or of a mixture of nitrogen dioxide and carbon disulphide. The electric spark will also bring about the union of the two gases. If a light glass flask be filled with equal measures of chlorine and hydrogen over the water trough, and the mixture be fired by the induction spark, a loud explosion results, and the flask will be shattered to fragments. The combination may be effected without danger by covering the flask with a thin wooden or sheet iron box (fig. 89). We have already given many illustrations of the powerful chemical affinity which chlorine manifests for hydrogen. It is noticed that the aqueous

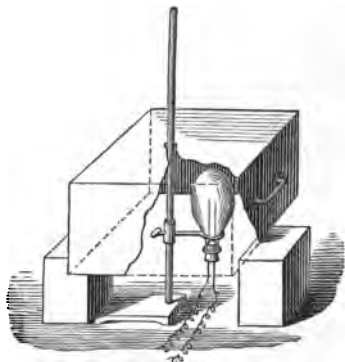
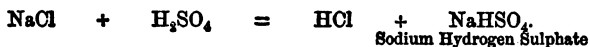


Fig. 89.

solution of the gas gradually loses its colour, not only from the dissipation of the gas, but also from the fact of its combining with the hydrogen of the water. The liberated oxygen, also, combines with a second portion of the chlorine to form chloric and perchloric acids. The decomposition of water by chlorine may be effected more quickly at a high temperature. If chlorine and steam be together passed through a porcelain tube, at a red heat, and the products of the reaction be collected over the pneumatic trough, the gas which is obtained will be found to be pure oxygen, the hydrochloric acid which is simultaneously formed being absorbed by the water.

Hydrochloric acid gas was discovered by Priestley in 1772. It may readily be prepared by the action of sulphuric acid upon common salt—



It may be collected over mercury, but not over water, as it is very soluble in that liquid. It is a colourless, irrespirable, incombustible gas, which does not support combustion. It possesses a penetrating odour, and fumes strongly in a moist atmosphere, owing to its intense affinity for water.

Under a pressure of about 40 atmospheres at 10°, hydrochloric acid may be condensed to a colourless liquid of specific gravity 1.27. It is remarkable that this anhydrous acid is without effect on iron, zinc, magnesium, lime, and even on certain carbonates, although an aqueous solution of the gas rapidly attacks these bodies.

Hydrochloric acid gas decomposes certain peroxides, especially when gently heated. If a stream of the dry gas be passed over heated manganese dioxide, water will be formed, together with chlorine, which will manifest itself by its peculiar colour, odour, and bleaching action. (Fig. 90).



If the manganous chloride be washed out of the bulb, and the solution mixed with slaked lime, and the precipitated oxide be treated with a stream of air, it is converted

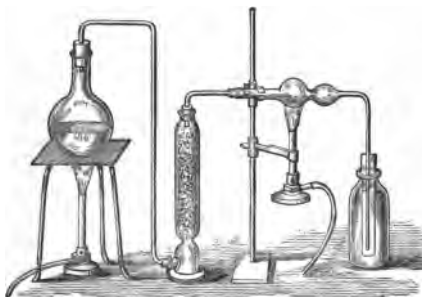


Fig. 90.

into a higher state of oxidation, and may again be used for the generation of chlorine. This is the principle of Weldon's process, which is extensively employed in the utilization of the "still liquors" of the bleaching powder manufactories.

Mr Deacon has made the interesting observation that if a

mixture of hydrochloric acid gas and oxygen be passed over cupric sulphate heated to about 400° , the hydrochloric acid is decomposed, its hydrogen combining with the oxygen to form water, whilst the chlorine is liberated. This principle constitutes the basis of a method of preparing chlorine on the large scale without the intervention of manganese dioxide.

At the ordinary temperature, water dissolves about 450 times its volume of hydrochloric acid gas. During the act of solution the liquid becomes heated, and increases considerably in bulk. The strongest solution has a sp. gr. of 1.21; it fumes strongly in the air, and gives off large quantities of the gas at a gentle heat. When the temperature of the liquid slightly exceeds 180° , hydrochloric acid and water distil over together in constant proportion. The distillate has a sp. gr. of 1.1, and contains 20.14 per cent. of the gas. The composition of the distillate varies with the pressure under which it is boiled; for each pressure there exists a corresponding aqueous acid, which distils unchanged so long as this pressure is maintained. Under the pressure 0.1 m., the acid of constant boiling point contains 22.9 per cent. HCl; under the pressure of 1.0 m., it contains 19.7 per cent.; and, under the pressure of 2 m., it contains 18.5 per cent.

The hydrochloric acid of the shops (commonly known as muriatic acid or spirit of salt) has generally a yellow colour, due to the presence of chlorine or ferric chloride. It not unfrequently contains sulphurous, sulphuric, and arsenious acids, derived from impurities in the oil of vitriol used in its manufacture. It is a powerful acid, reddens litmus strongly, dissolves many metals with loss of hydrogen, and gives rise to a series of important salts termed chlorides. The strong acid readily suffers electrolytic decomposition, the chlorine being evolved from the positive pole, and the hydrogen from the negative pole; indeed, this decomposition affords a ready means of demonstrating the composition of hydrochloric acid.

The elements may be arranged into two groups, depending upon the particular pole at which they make their appearance during the electrolysis of their compounds.

The elements which are evolved at the *positive* pole are called *electro-negative elements*; those which appear at the *negative* pole are termed *electro-positive elements*. There is, however, no absolute line of demarcation between the two groups, as they imperceptibly merge into each other. It is worthy of note that the stability of a binary chemical compound is in some degree related to the position in the electro-chemical series of its components: the more widely they diverge the greater is the stability, the more nearly they approximate the less striking are the manifestations of chemical action attending their union, and the more unstable is their combination.

144. Combinations of Chlorine with Oxygen.—By indirect means chlorine may be made to unite with oxygen in five proportions to form the following series of compounds:—

Chlorine Monoxide, Cl_2O .
 Chlorine Trioxide, Cl_2O_3 .

By the substitution of hydrogen for a moiety of the radicals, each of these oxides gives a corresponding acid, exactly as in the nitrogen series—

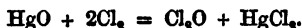
$\begin{array}{c} \text{Cl} \\ \text{Cl} \end{array} \left\{ \begin{array}{c} \text{O} \end{array} \right.$	$\begin{array}{c} \text{ClO} \\ \text{ClO} \end{array} \left\{ \begin{array}{c} \text{O} \end{array} \right.$	$\begin{array}{c} \text{N} \\ \text{N} \end{array} \left\{ \begin{array}{c} \text{O} \end{array} \right.$	$\begin{array}{c} \text{NO} \\ \text{NO} \end{array} \left\{ \begin{array}{c} \text{O} \end{array} \right.$
$\begin{array}{c} \text{Cl} \\ \text{H} \end{array} \left\{ \begin{array}{c} \text{O} \end{array} \right.$	$\begin{array}{c} \text{ClO} \\ \text{H} \end{array} \left\{ \begin{array}{c} \text{O} \end{array} \right.$	$\begin{array}{c} \text{N} \\ \text{H} \end{array} \left\{ \begin{array}{c} \text{O} \end{array} \right.$	$\begin{array}{c} \text{NO} \\ \text{H} \end{array} \left\{ \begin{array}{c} \text{O} \end{array} \right.$
Hypochlorous Acid.	Chlorous Acid.	Hyponitrous Acid.	Nitrous Acid.

And exactly as no acid is known corresponding to N_2O_6 , so also we find that the next oxide of chlorine, the chlorine tetroxide Cl_2O_6 , is a neutral substance. We know, however, of two acids of the chloroxygen series of which we have not obtained the corresponding anhydrides, viz.:—

Chloric acid, HClO_3 .
 Perchloric acid, HClO_4 .

145. Chlorine Monoxide, Cl_2O , molecular weight 87. This substance was discovered by Balard in 1834, and may

be prepared by passing a gentle stream of chlorine over well-cooled precipitated mercuric oxide—



The mercuric chloride combines with a portion of the un-attacked oxide to form a brown crystalline oxychloride. Chlorine monoxide is a yellow gas, heavier than air, and very prone to decomposition, especially in presence of sunlight. By the application of a freezing mixture the gas may be condensed to an orange-coloured liquid, which on the least elevation of temperature explodes, with the formation of two volumes of chlorine and one volume of oxygen.

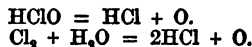
Chlorine monoxide is dissolved by water forming *hypochlorous acid*—



This acid may be obtained by the oxidation of hydrochloric acid. If air, saturated with hydrochloric acid, be passed through a warm solution of permanganic acid, and the liquid be then distilled, hypochlorous acid passes over: $\text{HCl} + \text{O} = \text{HClO}$. Hypochlorous acid may also be prepared by passing a stream of chlorine into water containing calcium carbonate in suspension—



The aqueous acid possesses a yellowish colour, and a characteristic chloroid smell. It gradually decomposes, especially if concentrated, into chloric acid, chlorine, oxygen, and water. The acid possesses a powerful bleaching action from the ease with which it gives up its oxygen; its action is indeed twice as energetic as that of an equivalent quantity of chlorine—



For the same reason the acid exerts a powerful oxidizing effect. Arsenic and iodine are rapidly converted by it into iodic and arsenic oxides. The metals act variously with this acid; some are converted into oxides with liberation of chlorine, others into oxichlorides, and a few into chlorides with liberation of oxygen. Hydrochloric and hypochlorous acids when mixed suffer mutual decomposition with the formation of water and free chlorine: $\text{HClO} + \text{HCl} = \text{H}_2\text{O} + \text{Cl}_2$.

Hypochlorous acid unites directly with *ethene* to form *glycolic chlorhydrin* $C_2H_4 \left\{ \begin{smallmatrix} OH \\ Cl \end{smallmatrix} \right.$ With oil of turpentine it forms a *dichlorhydrin* $C_{10}H_{16} \left\{ \begin{smallmatrix} (OH)_2 \\ Cl_2 \end{smallmatrix} \right.$ With benzene it forms *chlorobenzene* and water $C_6H_6 + HClO = C_6H_5Cl + H_2O$. By eliminating the hydrogen in hypochlorous acid by various electro-positive elements a series of salts, termed the *hypochlorites*, are obtained. These substances are very unstable; they gradually give off oxygen, and are converted into a mixture of chlorite, chlorate, and chloride. *Calcium hypochlorite* is the best known member of the series; it is obtained by the action of water upon *bleaching powder* or *chloride of lime*. This substance, which has the formula $Ca_3H_6O_6Cl_4$, does not contain preformed hypochlorite, but splits up into calcium hydrate, chloride, and hypochlorite and water—



146. Manufacture of Chloride of Lime.—This important substance is made by treating slaked lime with dry chlorine. The gas is generated from a mixture of manganese dioxide and hydrochloric acid, or from manganese dioxide, sulphuric acid, and common salt. The vessel in which the chlorine is generated is termed the “still;” the receptacles in which the lime is placed are called “the chambers,” or “receivers,” or “condensers.” The stills are usually made either of solid stone or of stone flags securely cemented together by a mixture of tar and china clay; the chambers are of lead, stone, or brick, and are of various forms and sizes. In a few localities lead is preferred by reason of the superior cooling action of the metal, as a low temperature promotes the formation of good bleaching powder; occasionally composite chambers are employed, the bottom being of stone, the sides and top of lead. Generally, however, the chambers are built of stone flags, and are arranged in rows in a building ventilated to allow of a current of air to pass between and around them in order to keep the stonework as cool as possible. Occasionally the chambers are fitted with shelves, upon which the slaked lime is placed to a depth of a few inches. These shelves are open alternately back and front, so that the chlorine traverses

one shelf after another. The doors of the chambers are fitted with windows in order that the process may be watched, and there are small openings in the sides to permit of the lime being stirred so as to present fresh surfaces to the gas. The choice of lime for the manufacture of bleaching powder is a matter of some importance, as the presence of even small quantities of iron gives a yellow colour to the product; the oxides of manganese are equally objectionable, as they appear to promote the spontaneous decomposition of the bleaching powder. The proper hydration of the lime is also of great importance; if too little water be present the lime is mainly converted into calcium chloride and chlorate, and but little of the bleaching compound is obtained; on the other hand, an excess of water retards the absorption of the chlorine, and reduces the ultimate strength of the product. The quick-lime is slaked soon after it is burnt; it is spread on the ground to a depth of from 6 inches to 1 foot, and is watered evenly over the surface, about 5 gallons of water being usually employed for each cwt. of lime. When slaked the lime is sifted, to remove any lumps.

We have already stated that attention must be paid to the temperature in absorbing the chlorine; if the absorption goes on too rapidly, a great amount of heat is developed, and much of the lime is converted into calcium chlorate. It is necessary, therefore, to conduct the operation slowly, and to give every facility for the dissipation of the heat produced in the chemical action. The time occupied in saturating the lime varies of course with the quantity and the temperature: 14 cwt. of lime requires from 36 to 48 hours, although, if the layer is thin, and the chamber cool, the absorption is occasionally complete in from 24 to 30 hours. The amount of available chlorine in the product varies from 30 to 39 per cent.

The constitution of bleaching powder has given rise to much discussion. The substance was formerly regarded as a mixture of calcium chloride and hypochlorite; but several facts militate against such a supposition. Calcium chloride is highly deliquescent, and like most deliquescent salts, it is soluble in alcohol; but bleaching powder, when properly manufactured, becomes moist only very gradually on ex-

posure to air, and alcohol does not dissolve any appreciable quantity of it. Chloride of lime is apparently a definite chemical combination, readily decomposed on treatment with water. Dry bleaching powder is unaltered in contact with excess of chlorine; but its solution, when acted upon by the gas, becomes strongly acid. If the excess of the chlorine be then removed by a current of carbon dioxide, the quantity of available chlorine (as hypochlorous acid) is found to be doubled—



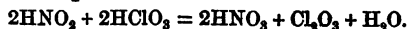
At a slightly elevated temperature dry bleaching powder is decomposed with separation of water and formation of calcium chlorate—



When bleaching powder is exposed to *moist* air, it is slowly decomposed with the evolution of *hypochlorous acid* by the action of atmospheric carbon dioxide. On account of the powerful oxidizing action of the hypochlorous acid, bleaching powder is extensively used as a disinfectant. By far the larger proportion of that manufactured is used for bleaching and clearing. The goods to be bleached are dipped in a solution of chloride of lime in water, and then in very dilute sulphuric or hydrochloric acid. Chlorine is thus evolved, which brings about the oxidation of the colouring matters.

Other bleaching compounds are occasionally used, as, for example, chloride of magnesia, chloride of soda or liquor of Labarraque, chloride of potash or water of Javelle (which was the first bleaching agent artificially prepared), and the hypochlorites of zinc and alumina.

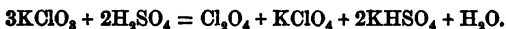
147. Chlorine Trioxide—symbol Cl_2O_3 ; molecular weight 119; density 59.5—was discovered by Millon, and may be prepared by heating a mixture of potassium chlorate, nitric acid, and arsenic trioxide. Chloric acid is liberated and is reduced by the nitrous acid formed by the action of the arsenic trioxide upon the nitric acid—



According to Brandau, the substance is more readily ob-

tained by the action of *sulphobenzolic* acid upon chloric acid. One part of benzene is dissolved in ten parts of sulphuric acid, previously diluted with its own weight of water, and the solution is heated to 50° with 1.2 parts of pulverized potassium chlorate, in a small flask furnished with a delivery tube fitted into its neck by grinding. On the neck are blown two or three bulbs, which are partially filled with water to wash the gas. The substance condenses in a freezing mixture to a reddish-brown mobile liquid of sp. gr. 1.38. The liquid is very prone to decomposition, and explodes at a temperature above 0° . The vapour is yellowish-green; it is decomposed by sunlight, and explodes when heated to 50° — 60° . It is soluble in water, forming at first a yellow crystalline hydrate; 100 parts of water dissolve about 5 parts of the oxide. The substance is gradually transformed into chlorous acid, HClO_2 , from which a number of unstable salts, termed *chlorites*, may be prepared; these are generally soluble in water, are crystallizable, and possess the property of bleaching.

148. Chlorine Tetroxide—symbol Cl_2O_4 —was discovered by Count Stadion, and may be prepared by the action of strong sulphuric acid upon potassium chlorate—



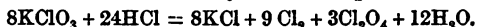
Potassium chlorate and sulphuric acid give chlorine tetroxide, potassium perchlorate, potassium-hydrogen-sulphate, and water. This gas may also be obtained, mixed with carbon dioxide, by heating a mixture of potassium chlorate and oxalic acid to a temperature of 70° . It possesses a bright yellow colour, and an aromatic odour. It may be condensed to a liquid in a freezing mixture, and by intense cold may be solidified. It is exceedingly explosive, being resolved into free chlorine and oxygen when slightly heated. It is slightly soluble in water, bleaches powerfully, and is absorbed by alkaline solutions with the formation of a chlorate and a chlorite—



a reaction analogous to that which occurs with nitrogen tetroxide (p. 201).

149. Euchlorine is the name applied to the product of the

reaction of hydrochloric acid upon potassium chlorate. This product was formerly supposed to be a definite oxide of chlorine, but later experiments have proved that it is a mixture; for, on passing the gas through a freezing mixture, it deposits chlorine tetroxide, whilst free chlorine is left uncondensed. The reaction may be thus represented—

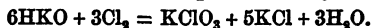


This mixture of chlorine and chlorine tetroxide constitutes a powerful oxidizing agent, and is frequently made use of in analytical chemistry, especially for the destruction of organic matter.

150. Chloric Acid—Symbol HClO_3 .—This acid is obtained by the gradual and spontaneous decomposition of aqueous solutions of the preceding oxides. It is more readily prepared in the pure state by the decomposition of a chlorate by means of dilute sulphuric acid. If barium chlorate in solution be mixed with dilute sulphuric acid in equivalent proportions, the following reaction ensues:—



The liquid decanted from the insoluble barium sulphate, and concentrated *in vacuo*, yields chloric acid as a colourless, syrupy liquid, of a chloroid smell, and strong acid reaction. When concentrated, it is readily decomposed, and on ebullition it is converted into perchloric acid and water with the evolution of chlorine and oxygen. From the ease with which it parts with oxygen, chloric acid exerts a powerful bleaching action. By the elimination of its hydrogen, by different bases, it forms a series of salts termed *chlorates*, the most important of which is the potassium chlorate. This salt may be prepared by passing a stream of chlorine into a warm concentrated solution of potassium hydroxide—



Potassium chlorate is but sparingly soluble in water; by concentrating the solution, the greater portion of the salt separates out, and, by repeated crystallization from water, it may be obtained free from admixed chloride.

Potassium chlorate is now generally made by the decomposition of calcium chlorate, by means of potassium carbonate

or sulphate. To form the calcium chlorate, milk of lime is heated to 65°C ., and is poured into a stone vessel fitted with inclined shelves, hollowed out on the under side so as to resemble an inverted shallow dish (fig. 91). The chlorine passes under the shelf *c* by means of an earthenware pipe, and there spreads itself out into a thin layer, which is rapidly absorbed by the milk of lime. The excess of the gas passes through the hole *d* to the under side of the shelf *e*, along which it makes its way; it is only to-

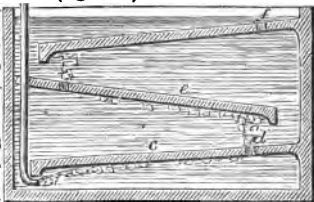


Fig. 91.

wards the end of the process that any chlorine escapes through *f*. The lime is kept in suspension by an agitator; when the process is at an end, the whole of the lime will be dissolved. The success of the operation depends upon the complete solution of the lime: so long as this remains undissolved, calcium hypochlorite is formed. Potassium sulphate is then added to the solution, and after standing it is concentrated until it has a sp. gr. of 1.32, when it is run into coolers to crystallize. The crystals are purified by successive recrystallizations, until they are free from potassium chloride.

Potassium chlorate crystallizes in anhydrous six-sided plates, which often attain to a considerable size. Water dissolves only 3.3 parts of the salt at 0° , and 6.03 parts at 15° . It is insoluble in alcohol. Respecting its decomposition by heat, see p. 63.

The applications of potassium chlorate depend on the facility with which it parts with oxygen. When triturated with sulphur or phosphorus in a mortar, it produces a sharp explosion. Antimony tersulphide takes fire when pulverized with the salt. The substance is extensively used in the manufacture of fireworks and lucifer matches. The composition employed in percussion caps consists of potassium chlorate, 26 parts; nitre, 30 parts; fulminate of mercury, 12 parts; sulphur, 17 parts; ground glass, 14 parts; gum arabic, 1 part. Attempts have been made to substitute potassium chlorate for nitre in the manufacture of gunpowder, but without success. The salt is also used to some extent by

the calico printer for heightening the intensity of steam colours.

151. Perchloric Acid—Symbol HClO_4 . This substance was discovered by Stadion, but its properties and derivatives have been mainly studied by Serullas and Roscoe. It may be obtained (1.) By the electrolysis of chloric acid; (2.) By boiling chloric acid; (3.) By the action of sulphuric acid upon the chlorates; and (4.) By the action of sulphuric acid upon the perchlorates. The aqueous acid may be concentrated by boiling in a retort until it acquires a temperature of 103° , when it distils over as an oily hydrate, containing 70.3 per cent. HClO_4 . The pure acid may be obtained by redistilling this product with strong sulphuric acid, as a colourless, oily, volatile liquid of sp. gr. 1.782, which fumes strongly in the air. It is an exceedingly powerful oxidizing agent, and sets fire to charcoal, paper, and other organic substances. It attacks the skin, producing very painful wounds, and when dropped into water it hisses like a hot iron. Its aqueous solution reddens litmus strongly, but exerts no bleaching action. It rapidly acts on zinc and iron, evolving hydrogen, and forming the perchlorates of those metals.

The perchlorates are, with the exception of the potassium salt, very soluble and deliquescent. This salt is indeed one of the most insoluble of the potassium compounds; perchloric acid has been proposed as a means of separating potassium from sodium, ammonium, &c.

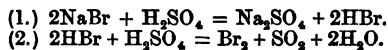
152. Bromine—Symbol Br ; atomic weight 80; density 80. —This element was discovered by Balard in the mother liquors of certain salt marshes in the south of France. It is contained in sea water and in the water of many mineral springs, in combination with calcium and magnesium. It is found in kelp, in sponges, and in many marine animals. Native bromide of silver occurs in Chili and in Mexico, and constitutes an ore of that metal. The magnesium and calcium bromides being highly soluble salts, remain in the solution obtained by concentrating sea or mineral waters. By

adding sulphuric acid and manganese dioxide, the salts are decomposed with formation of free bromine. On gently heating the solution the bromine volatilizes, and may be condensed in a well cooled receiver. The accompanying water dissolves about 3 per cent. of bromine, which may be extracted by agitating the liquid with ether or carbon bisulphide. On decanting the solution, rendering it alkaline with caustic potash and distilling, the ether may be recovered; the solution contains a mixture of bromide and bromate. By evaporating the liquid to dryness, and igniting the residue, the substance is wholly converted into potassium bromide. A simpler method of obtaining bromine from kelp will be described under Iodine.

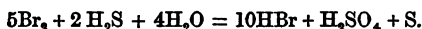
Bromine is a dark-red liquid of an exceedingly irritating odour, whence its name from *βρῶμος*, a stench. It is very poisonous, and rapidly attacks organic matter. It is 3.187 times heavier than water, boils at 59.6° , under a pressure of 751 m.m., and solidifies at -24.5 to a reddish-brown crystalline mass. If a tube partially filled with bromine be heated above a certain point, the whole of the bromine becomes quite opaque, and the tube has the appearance of being filled with a dark-red opaque resin (Andrews). The solution of bromine in water has a brownish-red colour; the amount of the halogen dissolved decreases with the temperature; at 5° the liquid takes up 3.6 per cent., and at 30° 3.126 (Dancer). A saturated solution has a density of 1.024. On cooling this solution, bromine hydrate $\text{Br}_2 \cdot 10\text{H}_2\text{O}$ separates out; this substance is possessed of considerable stability, even at ordinary temperatures. Bromine water is frequently employed in analysis as an oxidizing agent; its oxidizing action is due to its affinity for hydrogen; on this account the aqueous solution is slowly decomposed with formation of hydrobromic acid. This decomposition is greatly increased by passing a mixture of bromine vapour and steam through a red hot tube. Bromine attacks organic substances, such as cork, starch, the skin, &c., staining them yellow. In its general chemical deportment bromine strongly resembles chlorine; it gives rise to a variety of organic and inorganic compounds, which in their constitution and main properties are strictly analogous to the corresponding chlorides.

153. Hydrobromic Acid.—Symbol HBr ; molecular weight 81; density 40.5.—Although bromine unites with hydrogen it does not manifest the intense affinity for that gas which is so characteristic of chlorine. Bromine gas and hydrogen mixed in equal volumes may be exposed to the action of direct sunlight without explosion. A lighted taper may even be thrust into the mixture without any great amount of combination occurring, but union rapidly occurs on passing a series of electric sparks through the mixed gases, or on sending them through a red-hot tube.

Hydrobromic acid cannot readily be obtained by the action of sulphuric acid upon sodium or potassium bromide, since the product is contaminated with free bromine and sulphur dioxide, resulting from the action of the hydrobromic acid upon the heated sulphuric acid—

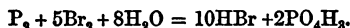


Hydrobromic acid, in solution, may readily be prepared by treating bromine water with sulphuretted hydrogen—



The liquid is filtered from the precipitated sulphur, and is distilled from the sulphuric acid.

Hydrobromic acid gas may be most advantageously prepared by the action of bromine on phosphorus suspended in water. One part of amorphous phosphorus is suspended in 15 parts of water, and gradually mixed with 10 parts of bromine. The following reaction ensues:—



Bromine, phosphorus, and water give hydrobromic and phosphoric acids. Hydrobromic acid gas may also be easily obtained by dropping bromine upon paraffin heated to 150° .

Hydrobromic acid is a colourless gas, which fumes strongly in the air, and excites violent coughing, from its irritable action on the fauces and air passages. It may be condensed to a liquid at -69° , and may be made to solidify at -73° . A fragment of potassium introduced into the gas decomposes it immediately, even in the cold, forming potassium bromide, and liberating half a volume of hydrogen; the gas is there-

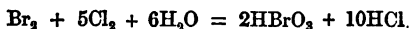
fore made up of 1 vol. of bromine and 1 vol. of hydrogen, united without condensation. Chlorine instantly decomposes the gas, eliminating the bromine; its aqueous solution is decomposed, in like manner, by chlorine. Iodine, however, is without action upon it. Metallic peroxides also decompose it exactly as in the case of hydrochloric acid.

Hydrobromic acid is rapidly absorbed by water; the strongest aqueous acid which can be obtained, boiling at a constant temperature under the ordinary pressure of the air, has a sp. gr. of 1.49, and contains 48.17 per cent. HBr; it fumes strongly in the air, and boils at 126°. (Roscoe: Topsoë).

154. Oxiacids of Bromine.—No oxide of bromine has yet been isolated, although three oxiacids have been obtained—viz., hydrobromous, bromic, and perbromic acids, corresponding to hypochlorous, chloric, and perchloric acids.

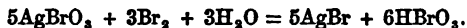
155. Hypobromous Acid.—Symbol HBrO .—The existence of this substance was inferred by Balard from the observation that bromine formed bleaching liquids corresponding to the hypochlorites with solutions of the alkalies and alkaline earths. A bleaching compound was also obtained by him by agitating mercuric oxide with bromine water; this body could be distilled *in vacuo*, and gave reactions similar to those of hypochlorous acid. These observations have been confirmed by Dancer, who has moreover shown that the same compound may be prepared by adding bromine to silver nitrate solution; half the bromine is precipitated as silver bromide, the other half remains in solution as hypobromous acid. Under a pressure of 5 c.m. hypobromous acid may be distilled at 50°; it is a straw coloured liquid of an acid reaction, it bleaches strongly, and decomposes when heated above 60°.

156. Bromic Acid, HBrO_3 , is the best known of the oxiacids of bromine. It may be obtained by methods similar to those employed for the preparation of chloric acid. It may also be prepared by passing a stream of chlorine through bromine water—



Potassium bromate may readily be prepared by passing bromine vapour into a solution of potassium carbonate previously saturated with chlorine gas. On heating the solution

and mixing it with silver nitrate the sparingly soluble silver bromate is precipitated. If this salt be suspended in water and treated with bromine, silver bromide and bromic acid are obtained in accordance with the equation—



Bromic acid solution has a strong acid reaction; it reddens litmus paper and ultimately bleaches it; at 100° it is decomposed into bromine and oxygen. The majority of the bromates are soluble, crystallizable salts; those of the alkalies are rapidly decomposed on heating into bromides and oxygen, without the intermediate formation of perbromates.

157. Perbromic Acid, HBrO_4 , may be obtained by the action of bromine upon perchloric acid. It is a colourless, oily liquid, which is not reduced by sulphurous or sulphydric acids. Indeed this substance appears to be the most stable of the oxiacids of bromine. The potassium salt is more soluble than the corresponding perchlorate. The barium and silver salts, unlike the bromates, are soluble in water, and crystallizable.

158. Iodine—Atomic weight 127; density 127.—This element was discovered in 1811 by Courtois in the mother liquor of kelp. In attempting to prepare nitre from the potash salts in the solution obtained by lixiviating this substance, Courtois observed that the copper apparatus was often attacked to a remarkable extent. This corrosive action he found to be due to an hitherto unknown substance, characterized by a beautiful violet-coloured vapour.

Iodine is never found free in nature; it exists principally in combination with potassium, magnesium, and calcium. It is very widely distributed, although it is seldom present in large quantity in any one spot. It has been found in certain zinc ores, and also in combination with silver and mercury. It may be detected in many dolomites and limestones. The sal-ammoniac contained in volcanic exhalations is occasionally mixed with ammonium iodide. Chili saltpetre often contains iodine, and this substance may sometimes be detected in the nitric acid prepared from this salt. The medicinal value of

many mineral waters is said to be due to the iodides which they contain. The mineral springs of Bonnington in Scotland, and those of Bath, Cheltenham, and Leamington in England, contain iodides of potassium, sodium, or magnesium. Sea water constitutes the great source of the iodine of commerce; it appears to exist therein as calcium iodate, the amount of which, however, according to Sonstadt, does not exceed 1 part in 250,000 parts of water. Marine plants have the power of assimilating the iodine, and on incinerating them, this substance remains in the ash as alkaline iodide. The quantity of the iodine contained in the various sea plants is by no means uniform, as the following determinations by Stanford prove:—

100 parts of dried *laminaria digitata* contain 0·47 parts of iodine.

100	"	"	<i>saccharina</i>	"	0·16	"
100	"	"	<i>fucus vesiculosus</i>	"	0·01	"
100	"	"	<i>nodosus</i>	"	0·04	"

The ash or *kelp* from sea weed collected on the coasts of Scotland and Ireland contains the largest proportion of iodine. Various marine animals also contain iodine, as, for example, the common sponge, the horse sponge, various species of *Tubularia*, oysters, herrings, &c. Cod liver oil is said to contain about 0·04 per cent. of iodine.

On the western and northern shores of Scotland, and on the adjacent islands, the collection and incineration of sea weed give employment to a large proportion of the population. In Scotland the weed is cut from June to September; it is spread out along the shore to dry, and is then burnt in shallow kilns. The combustion is regulated so that the mass of the ignited weed never actually bursts into flame, and care is taken to prevent the ash fusing until near the end of the operation. As soon as the greater portion of the carbonaceous matter is burnt away, the ash is raked together when it fuses, and forms a cake at the bottom of the kiln, technically known as a "floor," which varies from 3 to 6 inches in thickness, and the fused mass is broken up by throwing water upon it. The most valuable kelp is made from the *laminaria digitata*, which, when of good quality, yields from 10 to 15 lbs. of iodine per ton.

There are a number of disadvantages connected with this

method of incinerating the weeds. The high temperature of the burning mass occasions loss of iodine and of potash (one of the most valuable constituents of the kelp), and the crude manner in which the weed is burned leads to admixture, and even to direct adulteration, with clay, sand, &c. The kelp burner can only work during the summer months, and consequently the winter supply of weeds is neglected. The weeds obtained in winter consist principally of deep sea algae, torn up by storms, and contain iodine and potash in largest quantity. Mr. Stanford has improved the process by drying the weeds under cover, compressing them into cakes by hydraulic pressure, and heating them in iron retorts at a low red heat. Gas of considerable illuminating power is given off, which is collected in gasometers; and utilized as a source of heat, and a quantity of ammonia is formed which condenses in the aqueous portions of the distillate. The charcoal in the retorts contains the whole of the iodides and potash salts, which are extracted by lixiviation with water. This charcoal also contains about 20 per cent. of earthy phosphates, and possesses considerable disinfecting and decolorizing properties.

The solution is run into evaporating pans and concentrated, and the potassium sulphate which crystallizes out is removed by means of perforated ladles. When sufficiently concentrated, the liquid is run into cooling vats, when potassium chloride separates out. The mother-liquor, containing all the iodides and bromides, is mixed with oil of vitriol, and after standing, is transferred to the iodine still (fig. 92). This apparatus consists of an iron still, surrounded by brick work, and fitted with a movable leaden cover, which can be lifted by means of a chain worked from a winch placed at the end of the row of stills. To the cover of each still are fitted two leaden pipes *a a*, each connected with a series of condensers, one of which is shown separately at A. After the introduction of the liquor containing the iodine and bromine, the covers are luted with clay, the pipes *a a* are fitted into their receptacles, and connected with the condensers. Manganese dioxide is thrown into the still through the hole *b*, which can be closed by a stopper. The stills are heated by separate fires; the iodine condenses in the receivers, and the accompanying water

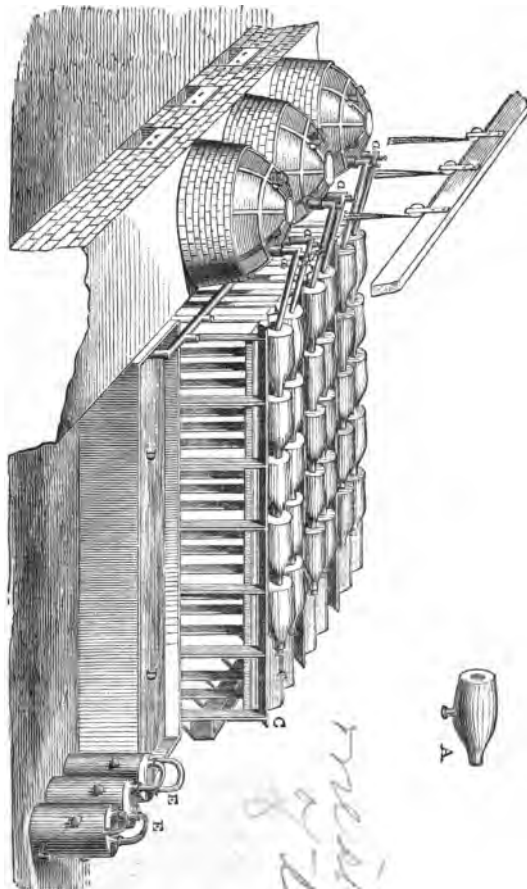
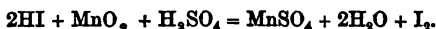


Fig. 92.

escapes through a tubulus at the bottom of each receiver (seen in A), and runs away along the channel C.

When no more iodine distils over (which can be determined by opening the stoppers *s s*, placed in the leaden pipes *a a*), the pipes *a a* are removed, and the still is connected with the main pipe *B*. More manganese dioxide is added, when the bromine is evolved; it is condensed in a leaden pipe coiled in the trough D D, and in the series of condensers E E, from which it is drawn off, and without further purification sent into the market.

The following equation represents the reaction of the manganese dioxide upon the acidulated liquid:—



The iodine may be partially purified by resublimation; it is placed in large stoneware bottles, surrounded by steam or boiling water, and connected by a leaden pipe with receivers, in which the vapours are condensed. Simple resublimation is not sufficient to effect the complete purification of iodine; as sent into commerce it invariably contains more or less chloride, and bromide, and cyanide of iodine. The quantity of the latter substance is occasionally as high as 30 per cent.

At ordinary temperatures iodine is a solid, crystallizing in rhomboidal plates of a greyish-black colour, and possessing a lustre resembling that of graphite. In thin leaves the crystals are transparent, and appear of a deep red colour; their specific gravity is 4.95. Iodine melts at 107° , and boils at 175° , but it volatilizes slightly at ordinary temperatures. Its vapour generally appears to be violet, whence its name from *lav*—violet; but in reality it is *dichroic*. Its colour is due to its power of transmitting the red and blue rays of the spectrum, and absorbing the green rays; if, however, the iodine vapour be sufficiently dense, the red rays are also arrested, and the vapour appears of a blue colour (Andrews). Iodine gives the heaviest vapour known; it is 127 times heavier than hydrogen, and more than $8\frac{1}{2}$ times heavier than air.

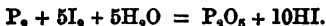
Iodine dissolves but sparingly in water (1 part in 7,000 of water); but it is readily dissolved by alcohol ether and carbon bisulphide. Its solution in the latter liquid exhibits the

dichroism of the vapour. Its colour appears to be purple or blue by transmitted light, according to its richness in iodine. The alkaline iodides also dissolve iodine in large quantity. If a strong solution of iodine in potassium iodide is mixed with water, chemically pure iodine is precipitated (Stas). Lugol's solution is made by dissolving 20 grains of iodine in 30 grains of potassium iodide contained in an ounce of water.

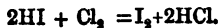
Iodine is used in medicine as a tonic, and by virtue of its peculiar action in effecting the absorption of glandular swellings. When swallowed in quantity it causes death from ulceration of the mucous membrane of the stomach.

Iodine forms an exceedingly characteristic blue colour with starch. This reaction is so delicate that $\frac{1}{450,000}$ part of iodine may be detected by means of starch. The nature of the blue substance is but imperfectly understood. It appears not to be a definite chemical compound. The iodine and starch probably stand to one another in a relation similar to that in which the colouring matters of lakes stand to the inorganic materials employed to precipitate them. On heating the blue liquid to 80° it is decolorized; the colour, however, reappears as the solution cools.

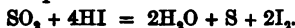
159. Hydriodic Acid—Symbol HI; molecular weight 128; density 64.—Iodine and hydrogen do not combine at the ordinary temperature; but, on volatilizing iodine in a stream of hydrogen, and heating the mixture to redness, hydriodic acid is readily formed. The two substances may be made to unite under the influence of spongy platinum. Hydriodic acid gas may easily be made by the action of water upon a mixture of iodine and amorphous phosphorus.



It is a colourless gas, which fumes strongly in the air, and reddens litmus. It is very soluble in water, but may be collected over mercury. It is incombustible, and a non-supporter of combustion. By the application of cold and pressure it may be liquefied; and at -51° it solidifies to a clear, transparent, ice-like mass. When mixed with chlorine or bromine, the gas is immediately decomposed with separation of iodine.



Sulphur dioxide and hydriodic acid, when mixed together, suffer mutual decomposition.



The aqueous solution of the gas is now frequently employed in chemical research; it may be conveniently prepared by



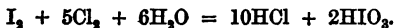
Fig. 93.

means of the apparatus seen in fig. 93. The flask *a* contains the mixture of red phosphorus and iodine; the water is added in small quantities at a time through the tap funnel *b*. The flask is connected with the tubulus of the retort *c*, the neck of which dips beneath the surface of water contained in the Woulf's bottle *d*. This arrangement prevents the possibility of the water employed to absorb the gas rushing over into the flask. The solution may also be obtained by passing a stream of sulphuretted hydrogen into water containing finely divided iodine; in a short time the hydriodic acid formed dissolves the remainder of the iodine, whereby the reaction is considerably accelerated. On distilling the solution, perfectly pure hydriodic acid is obtained. The strongest hydriodic acid solution which can be distilled under the ordinary pressure of the air boils at 127° , and has a specific gravity of 1.67. The concentrated acid fumes strongly in the air, and gradually becomes brown from separation of iodine.

160. Combinations of Iodine and Oxygen.—Two oxiacids of iodine are known, viz., iodic acid, HIO_3 , and periodic acid, HIO_4 , but only one of the corresponding anhydrides, viz., I_2O_5 , has been prepared. An acid analogous to hypochlorous acid appears to exist, although all attempts to isolate it have hitherto failed. It appears to be

produced in combination with potassium when iodine is added to a solution of potash, the formation of potassium iodate being preceded by that of the hypoiodite, as in the case of chlorine. The salt is even more unstable than the hypochlorite, and is quickly resolved into iodate and iodide. (Schönbein: Lenssen and Löwenthal.)

161. Iodic Acid.— HIO_3 ; molecular weight 176.—Sodium iodate occurs naturally, associated with sodium nitrate in Chili saltpetre, and iodic acid is occasionally found in nitric acid which has been prepared from this salt. Iodic acid is also formed in the electrolysis of aqueous hydriodic acid, or of water containing iodine in suspension. It may more readily be obtained by the action of strong nitric acid upon iodine, or by passing a stream of chlorine into water containing finely divided iodine—



Iodic acid crystallizes in transparent six-sided tables, which are very soluble in water. The solution reddens litmus, and then bleaches it. It has no action upon starch, but by the cautious addition of certain deoxidizing agents iodine is eliminated, which imparts a blue colour to starch. An excess of the reducing agent in certain cases destroys the colour from the formation of hydriodic acid; thus, in the case of sulphurous acid—



Iodic acid is reduced by morphine, with formation of iodine. This reaction is occasionally used as a test for the alkaloid. The solid substance suspected to contain morphine is moistened with a solution of iodic acid, and mixed with starch liquor, when a blue colour will be produced if the alkaloid be present.

Iodic acid, heated to 130° , parts with a quantity of water, and is converted into the compound $\text{I}_2\text{O}_5 \cdot \text{HIO}_3$. If this be heated to 170° it is completely resolved into iodine pentoxide, I_2O_5 . At a still higher temperature the anhydride is decomposed into oxygen and iodine. When dissolved in water it forms iodic acid.

Iodic acid is monobasic, and forms a series of well defined and stable salts, the greater number of which are insoluble

in water. The alkaline salts especially have a great tendency to unite with the pentoxide. Other three potassium iodates are known, viz. :—

Normal Potassium Iodate,	KIO_3 .
Potassium Di-iodate,	$2\text{KIO}_3, \text{I}_2\text{O}_5$.
Potassium Tri-iodate,	$2\text{KIO}_3, 2\text{I}_2\text{O}_5$.

Analogously constituted sodium compounds have been obtained.

Silver iodate is white, insoluble in water and nitric acid, readily soluble in ammonia. The solution, mixed with sulphurous acid, gives a yellow precipitate of silver iodide. The salt is decomposed by hydrochloric acid, with formation of silver chloride, iodine chloride, and free chlorine. Barium iodate, $2\text{BaIO}_3\cdot\text{H}_2\text{O}$, is also sparingly soluble in water and nitric acid; it is readily decomposed by hydrochloric acid, with formation of a dark-yellow coloured solution. The alkaline iodates are decomposed when heated with elimination of the whole of the oxygen and formation of iodides; the salts of the heavy metals, as those of zinc and iron, form oxides when ignited, iodine being expelled.

162. Periodic Acid— HIO_4 ; molecular weight 192.—This acid cannot be obtained by heating the alkaline iodates, as in the case of the corresponding chlorine compound, since these salts are directly converted into iodides without the intermediate formation of periodates. Periodic acid is most readily prepared by adding 1 part of iodine to 7 parts of sodium carbonate dissolved in 100 parts of water, heating the liquid, and passing a stream of chlorine into it until the formation of the sparingly soluble disodium periodate ceases. The precipitate is dissolved in nitric acid (free from nitrous acid), and mixed with silver nitrate, heated, concentrated, until mono-silver periodate AgIO_4 crystallizes out. By treating this compound with cold water it gives up half its acid, forming diargentate periodate; the solution yields periodic acid on concentration. It forms colourless crystals of the composition $\text{HIO}_4\cdot 2\text{H}_2\text{O}$. They melt at 130° , and at a somewhat higher temperature are resolved into iodine pentoxide, oxygen, and water. Neither the heptoxide, I_2O_7 , nor the monohydrated acid, HIO_4 , is known. The basicity of periodic acid is not yet definitely established. Many of the periodates

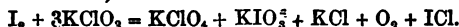
appear to have a very complicated constitution. The composition of a few of the principal salts is given below—

Normal Potassium Periodate	KIO_4 .
Tetra-potassium Periodate,	$\text{K}_4\text{I}_2\text{O}_9 + 9\text{H}_2\text{O}$.
Normal Silver Periodate,	AgIO_4 .
Tetra-argentic Periodate,	$\text{Ag}_4\text{I}_2\text{O}_9$.
Penta-argentic Periodate,	Ag_5IO_6 .
Di-barium Periodate,	$\text{Ba}_2\text{I}_2\text{O}_9 + 7\text{H}_2\text{O}$.
Normal Calcium Periodate,	CaI_2O_8 .
Di-calcium Periodate,	$\text{Ca}_2\text{I}_2\text{O}_9 + 9\text{H}_2\text{O}$.
Deca-mercurous Periodate,	$\text{Hg}_{10}\text{I}_2\text{O}_{12}$.

COMBINATIONS OF THE HALOGENS WITH ONE ANOTHER.

163. Chloride of Bromine.—Bromine rapidly absorbs chlorine, and forms an orange-coloured highly volatile liquid, the exact composition of which is unknown. It dissolves in water, and on strongly cooling the solution a crystalline hydrate of bromine chloride separates out. It melts at 7° , and is decomposed by exposure to sunlight, or more quickly by alkalis with formation of hydrochloric and bromic acids.

164. Iodine Monochloride, ICl , may be obtained by the direct union of its elements, or by heating iodine with potassium chlorate,



It is a highly volatile, dark-red, oily liquid, which congeals when touched with a solid substance to large red transparent prisms; the solid modification melts at 25° , and boils at about 101° . It deliquesces in the air, and is gradually decomposed by water; it gives no blue colour with starch; with aqueous ammonia it yields iodamide. It forms crystallizable compounds with the hydrochlorides of many vegeto-alkaloids.

Iodine trichloride, ICl_3 , is prepared by heating iodic anhydride in dry chloride of hydrogen; the iodic anhydride liquefies and is converted into iodine trichloride, which solidifies in long orange-yellow needles—



It melts at 25° — 30° , and gives off chlorine gas, which it reabsorbs on cooling. It has no action on starch.

165. Iodine Tetrachloride, ICl_4 , is said to be formed by the spontaneous decomposition of the monochloride, $4\text{ICl} = \text{ICl}_4 + \text{I}_3$; it is solid, and crystallizes in octahedra.

Iodine pentachloride, ICl_5 , is also said to exist.

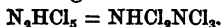
Iodine bromides, IBr and IBr_5 , are believed to exist; the former is a solid substance, the latter a liquid.

The combinations of the halogens among themselves are exceedingly indefinite; they illustrate in a remarkable manner the fact that the compounds of elements which closely approximate in the electro-chemical series are of a very unstable character. From the ease, however, with which they decompose, they often set up chemical reactions when the elements singly are inactive. Thus carbon tetrabromide is only formed when the carbon bisulphide is heated with bromine in presence of iodine,—i. e., with iodine bromide. The bromination of many hydrocarbons is often greatly facilitated by the presence of a small quantity of iodine in the bromine employed.

COMBINATIONS OF THE HALOGENS WITH NITROGEN.

166. Nitrogen Terchloride (NCl_3 ?), discovered by Dulong in 1812, may be prepared by the action of chlorine upon a solution of sal-ammoniac— $\text{NH}_4\text{Cl} + 3\text{Cl}_2 = 4\text{HCl} + \text{NCl}_3$. This mode of formation has already been mentioned (see nitrogen, p. 165). The compound may also be obtained by suspending a piece of ammonium chloride in a solution of hypochlorous acid— $\text{NH}_4\text{Cl} + 3\text{HClO} = \text{HCl} + \text{NCl}_3 + 3\text{H}_2\text{O}$.

This substance is a limpid, yellow, highly volatile oil of sp. gr. 1.65. It is readily decomposed with a violent explosion at a gentle heat, or when mixed with fat, or with many other organic substances. On account of its extreme instability, it has not been thoroughly examined. According to several observers, it would appear to contain hydrogen. Gladstone assigns to it the composition—

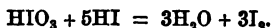


The corresponding *bromine compound* may be obtained by the action of potassium bromide upon the terchloride. It is

a heavy, dark-red, and exceedingly unstable liquid, which explodes violently in contact with phosphorus, oil of turpentine, &c. These substances are, in all probability, formed by the gradual replacement of the hydrogen in ammonia by the halogen—



167. Iodamides.—These compounds may, in like manner, be regarded as ammonia, in which more or less of the hydrogen has been replaced by iodine. They are prepared by digesting iodine in aqueous ammonia, or by adding a large excess of alcoholic ammonia to an alcoholic solution of iodine, and then diluting with water, or by adding potassium iodide to the so-called chloride of nitrogen. They are brownish-black powders which decompose with explosion when heated or when touched with a solid body. When moist, they slowly decompose, forming iodic and hydriodic acids and nitrogen. The two acids are then mutually decomposed, with formation of water and free iodine—



In presence of excess of ammonia this decomposition is retarded.

168. Iodammonium (NH_3I ?).—This body was prepared by Millon, by the action of ammonia gas upon iodine. Dry iodine absorbs about 9 per cent. of ammonia gas, and forms a viscid black liquid of a metallic aspect. It dissolves in alcohol, and is decomposed by water, with formation of ammonium iodide and di-iodamide—



169. Iodammonium Iodide, $\text{NH}_3\text{I}_2 = \text{NH}_2\text{I.I.}$, was obtained by Guthrie by adding finely powdered iodine to a saturated solution of ammonium carbonate or nitrate mixed with potash. It forms a brownish-black, mobile liquid, which decomposes on heating into iodine and iodammonium. It is decomposed by water, with separation of iodine, nitrogen, ammonium iodide, and di-iodamide, which explodes spontaneously as it is formed. The substance dissolves in alcohol, ether, chloroform, and carbon bisulphide without decomposition.

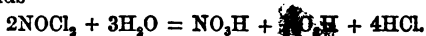
COMBINATIONS OF THE HALOGENS WITH OXYGEN AND
NITROGEN.

170. Nitryl Chloride, NO_2Cl , is obtained by the action of phosphoryl trichloride on silver nitrate. It is a light yellow oil, which boils at 5° , and remains liquid at -31° . It is decomposed by water with formation of nitric and hydrochloric acids.

171. Nitrosyl Monochloride, NOCl , is formed by the direct union of nitrogen dioxide, and chlorine. It is a deep orange-coloured gas, which condenses in a freezing mixture to a red fuming liquid, and is decomposed by water with formation of nitrous and hydrochloric acids. It does not attack gold or platinum, but is readily decomposed by mercury, forming calomel and nitrogen dioxide; $2\text{NOCl} + \text{Hg}_2 = 2\text{NO} + \text{Hg}_2\text{Cl}_2$. It is also obtained by the mutual action of nitric and hydrochloric acids (*vide infra*).

172. Nitrosyl Dichloride, NOCl_2 , is formed by gently heating a mixture of 1 part strong nitric acid with 3 parts hydrochloric acid. By passing the evolved gases through a tube cooled by a mixture of ice and salt, the nitrosyl chloride condenses, whilst the free chlorine which is simultaneously formed escapes.

Nitrosyl di-chloride is a clear, red, fuming liquid which boils at -7° , producing a deep yellow vapour. It is decomposed by water with formation of nitric, nitrous, and hydrochloric acids—



It does not act upon gold or platinum.

173. Aqua-Regia, or Nitrohydrochloric Acid, is formed by adding 1 part of nitric to 3 parts of hydrochloric acid. The mixture quickly becomes yellow, and eventually orange red, and evolves nitrosyl chlorides and free chlorine. This mixture of acids derives its name of *aqua-regia* from its power of dissolving the noble metals, gold, platinum, and the so-called platinum metals, which are unattacked by either of the acids separately. Its solvent effect is due to the formation of *nascent chlorine*, and not to the nitrosyl chlorides, which are without action upon the metals (*vide supra*). Aqua-regia is

frequently used in analytical chemistry, by reason of its powerful oxidizing action: many organic compounds are completely destroyed by it, and the greater number of sulphides are converted into sulphates or chlorides when heated with it.

No nitryl or nitrosyl bromides or iodides are known.

CHAPTER XI.

COMBINATIONS OF THE HALOGENS WITH CARBON.

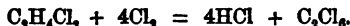
Chlorine does not unite directly with carbon, but several combinations of the elements may be obtained by indirect means. We have already seen that when a mixture of methane, CH_4 , and chlorine is exposed to direct sunlight, hydrochloric acid is formed, and chlorine replaces the eliminated hydrogen atom by atom, forming the following series of compounds:—



174. Carbon Tetrachloride CCl_4 (*Perchlorinated Methyl Chloride, Perchloroformene*).—This substance was discovered by Regnault, and may be obtained, as just stated, by the action of chlorine upon marsh gas or chloroform. It is now prepared on a large scale by the action of chlorine upon carbon disulphide. Chlorine mixed with carbon disulphide vapour is passed through a red hot porcelain tube; carbon tetrachloride and sulphur chloride are produced— $\text{CS}_2 + 4\text{Cl}_2 = \text{CCl}_4 + 2\text{SCl}_2$. The orange-coloured distillate is agitated with milk of lime to destroy the sulphur chloride; the carbon tetrachloride is decanted off and rectified. It is a limpid, colourless, highly refractive liquid of specific gravity 1.56. It boils at 77° . Its vapour, mixed with hydrogen and passed through a red hot tube, yields methane and ethene, together with hydrochloric acid. It is insoluble in water, but readily soluble in alcohol and ether. Its alcoholic solution treated with sodium or potassium amalgam yields *chloroform*, CHCl_3 , *monochlorinated methyl chloride*, CH_2Cl_2 , and *marsh gas*. This reaction is interesting as constituting a method of performing

the inverse series of changes to those by which the tetrachloride is produced; hydrogen gradually replacing chlorine. Chloroform may also be obtained from carbon tetrachloride by the action of zinc and hydrochloric acid. Its vapour possesses anæsthetic properties; the liquid is employed as a solvent for fats, resins, &c.

175. Carbon Trichloride, C_2Cl_6 , was discovered by Faraday, and is obtained, together with the dichloride, by passing the vapour of the tetrachloride through a tube heated to dull redness. It may also be prepared from ethane by the action of chlorine, at a gentle heat or in bright sunlight. The first effect is the formation of ethene dichloride (Dutch liquid), $C_2H_4Cl_2$; the subsequent action of the halogen is to eliminate the hydrogen. The ultimate reaction may be thus represented—



Carbon trichloride crystallizes in colourless, shining prisms, which have a peculiar aromatic odour, resembling that of camphor. The substance volatilizes at ordinary temperatures, melts at 160° , and boils at 182° . It burns in the flame of a gas lamp, and is decomposed when heated with tin or zinc, forming a metallic chloride and depositing carbon. When heated with potassium hydroxide to 210° in a sealed tube, it yields potassium oxalate and chloride—

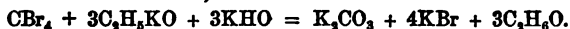


176. Carbon Dichloride, C_2Cl_4 , was also discovered by Faraday, and may be obtained by passing either of the preceding compounds through a red hot tube. It may likewise be prepared by the action of nascent hydrogen on the trichloride. It is a mobile liquid of specific gravity 1.619. It boils at 117° , and remains liquid at -18° . The liquid absorbs nitrogen tetroxide, forming a volatile crystalline compound, termed *dinitro-tetrachlorethane*, and having the composition $C_2Cl_4N_2O_4$. This substance is insoluble in water, but dissolves in alcohol and ether. It is decomposed at 140° into the dichloride and nitrogen tetroxide.

177. Hexachlorobenzene, C_6Cl_6 , was formerly regarded as carbon monochloride, C_2Cl_2 , until a determination of its vapour density established its true composition. It stands to that

compound in exactly the same relation that benzene stands to ethine. It may be prepared from benzene by the prolonged action of chlorine, or more readily by passing chloroform vapour through a red hot tube. It crystallizes in white silky needles, melts at 226° , but begins to sublime at a much lower temperature, and boils at 331° . It is an exceedingly stable compound, resisting even the action of boiling nitric acid. It is insoluble in water, but dissolves readily in hot alcohol.

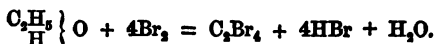
178. Carbon Tetrabromide, CBr_4 , is obtained by the action of bromine in presence of iodine bromide upon carbon disulphide. It is a white crystalline substance of an aromatic odour, melts at 91° , is insoluble in water, but dissolves easily in alcohol, ether, benzol, &c. Its alcoholic solution is decomposed on heating into aldehyde and hydrobromic acid. It is decomposed by alcoholic potash with formation of potassium bromide and carbonate, and alcohol—



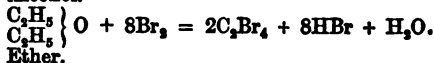
When treated with water and sodium amalgam it yields bromoform, CHBr_3 , and methylene dibromide, CH_2Br_2 (Bolas and Groves).

179. Carbon Tribromide (C_2Br_6), or Tetrabromethylene Dibromide ($\text{C}_2\text{Br}_4\text{Br}_2$), is a white crystalline solid, obtained by the action of bromine upon carbon dibromide (*vide infra*), which decomposes on heating into bromine and carbon dibromide. It is but slightly soluble in alcohol and ether.

180. Carbon Dibromide, C_2Br_4 , may be obtained by the prolonged action of bromine upon ether or alcohol—



Alcohol.



Ether.

It forms white crystalline plates of a satiny lustre and aromatic odour. It melts at 50° , and may be sublimed unchanged. It is insoluble in water, but readily soluble in alcohol; its solution is not acted upon by potash.

A liquid bromide of carbon is occasionally found in crude bromine. It is a colourless, oily liquid of sp. gr. 2.436. It

boils at 120° , and remains liquid at 20° . When heated with potassium hydroxide it yields a mixture of potassium bromide and carbonate.

181. Carbon Chlorobromide, or Tetrachlorethylene Dibromide, $C_2Cl_4Br_2$, is obtained by adding bromine to carbon dichloride, and exposing the mixture to light. It is a crystalline substance resembling carbon trichloride, of sp. gr. 2.3. Its relation to Dutch liquid, tetrachlorethylene, dichloride, and tetrabromethylene dibromide, is evident from the following formulæ:—

$C_2H_4Cl_2$	$C_2Cl_4Cl_2$	$C_2Cl_4Br_2$	$C_2Br_4Br_2$
Ethylene Dichloride.	Tetrachlorethylene Dichloride.	Tetrachlorethylene Dibromide.	Tetrabromethylene Dibromide.

No compound of iodine and carbon is known.

COMBINATIONS OF THE HALOGENS WITH CARBON AND HYDROGEN.

182. Chloroform (*Dichlorinated Methyl Chloride, Trichloromethane*), $CHCl_3$, was discovered by Souberan in 1831, although there is some evidence for believing that it was known long before that time. It is prepared on the large scale for use in medicine by distilling alcohol with chloride of lime. When pure it is a colourless oil of sp. gr. 1.525 at 0° . It boils at 61° , and remains liquid at -16° . It may be solidified, however, by its own evaporation. It is an agreeable aromatic odour, and a sweet spirituous taste. Inhaled in small quantity, its vapour causes excitement, but in larger quantity it occasions a kind of coma—an effect first observed by Sir J. Y. Simpson. On account of this action, chloroform is extensively used for producing insensibility to pain in surgical operations. Care is necessary to ensure its purity when so administered. It is occasionally contaminated with ether, alcohol, and empyreumatic substances. These are present in largest quantity in the chloroform prepared from methylated alcohol. The substance made from this source is apt to produce unpleasant after-sensations when inhaled. The presence of alcohol in chloroform is readily detected by shaking it with a solution of potassium bichromate acidulated with sulphuric acid, when the liquid becomes green owing to the formation of chromium sesquioxide. The presence of empyreumatic oils may be

recognized by the disagreeable odour left after the evaporation of the chloroform.

Chloroform is dissolved to a slight extent by water, which acquires its taste and odour. It is completely miscible with alcohol and ether. It dissolves sulphur, iodine, and phosphorus, and many vegeto-alkaloids, particularly quinine, narcotine, and atropine.

Chloroform decomposes slightly when exposed to light, with the formation of hydrochloric acid. This decomposition is retarded by keeping the liquid under water. Chloroform is also decomposed when passed through a red-hot tube, with liberation of chlorine, carbon, and hydrochloric acid, $\text{CHCl}_3 = \text{C} + \text{Cl}_2 + \text{HCl}$. This decomposition may be employed to detect chloroform in blood. A quantity of the blood is heated in a flask placed in the water-bath, and the chloroform vapour is passed through a tube heated to redness. The formation of the chlorine may be recognized by its power of turning iodized starch paper blue.

Chloroform forms *cuprous oxide* when heated with an alkaline solution of cupric oxide—



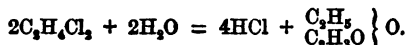
This reaction may be used as a test for chloroform; one drop of this liquid agitated with 100 c. c. of water immediately produces a red precipitate when heated with the copper solution.

183. Bromoform, CHBr_3 , may be obtained by the joint action of bromine and caustic potash on alcohol, or by decomposing bromal with alkalis. It is a mobile liquid of sp. gr. 2.13, and possesses the odour and taste of chloroform. It is less volatile than chloroform, and is more readily decomposed. When heated with aqueous solution of potash it splits up into formate and bromide of potassium.

184. Iodoform (*Di-iodated Methyl Iodide*), CHI_3 , was discovered in 1824 by Serullas, who regarded it as an iodide of carbon. It is readily obtained by heating iodine with alcohol, mixed with a solution of sodium carbonate. It may also be obtained by adding bleaching powder to a warm alcoholic solution of potassium iodide; calcium iodate and iodoform are

simultaneously produced. The iodoform may be separated by alcohol, in which it readily dissolves. Iodoform crystallizes in yellow, shining plates, which have the odour of saffron. It melts at about 117° , but is decomposed at a higher temperature. Treated with bromine it yields a colourless liquid, which solidifies at 0° to a crystalline mass resembling camphor; it is very volatile, and has a penetrating odour and sweet taste. It has the composition CHIBr_2 , and may be termed *dibrominated methyl iodide*.

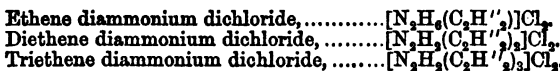
185. Ethene Dichloride (*Ethylene Dichloride*), $\text{C}_2\text{H}_4\text{Cl}_2$.—This compound is also known as Dutch liquid, from the fact of its having been discovered in 1795 by four Dutch chemists—Deiman, Paets van Troostwyk, Bondt, and Lauwerenburgh. It is readily obtained by mixing ethene with moist chlorine (compare p. 220). It is a colourless, oily liquid, of an ethereal odour and sweet taste. Its specific gravity is 1.256; it boils at 82° ; its vapour is inflammable, and burns with a green flame. When covered with water and exposed to light it yields hydrochloric acid and ethyl acetate—



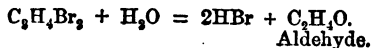
It is violently decomposed by potassium with formation of potassium chloride, ethene, chlorethene, and hydrogen (Maumené)—



Alcoholic ammonia heated in sealed tubes with ethene dichloride yields the following compounds:—



186. Ethene Dibromide, $\text{C}_2\text{H}_4\text{Br}_2$, is formed by the direct union of ethene and bromine. It is a colourless, aromatic liquid, boiling at 129° , and solidifying at about 0° . In its chemical relations it resembles the dichloride. When heated with water in sealed tubes it is converted into *aldehyde* and hydrobromic acid—



187. **Ethene Di-iodide**, $C_2H_4I_2$, is readily made by passing a stream of ethene gas over gently heated iodine; the product is washed with dilute solution of potash to remove excess of iodine, and is recrystallized from alcohol. It crystallizes in colourless needles, which melt at 75° with partial decomposition.

188. **Ethene Iodochloride**, C_2H_4ICl , is obtained by the action of a mixture of chlorine and iodine upon the preceding compound. It is a colourless, oily liquid, of a sweet taste, boiling at about 147° .

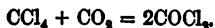
These substances give rise to an important series of derivatives, for an account of which the volume on *Organic Chemistry* must be consulted.

COMBINATIONS OF THE HALOGENS WITH CARBON AND OXYGEN.

189. **Carbonyl Chloride** (*Carbon Oxychloride*, *Phosgene*)—symbol $COCl_2$; molecular weight 99; density 49.5.—This compound is readily formed by mixing equal volumes of carbon monoxide and chlorine, and exposing the mixture to bright sunlight. It may also be obtained, together with carbon dioxide, by heating carbon tetrachloride with zinc oxide to 200° .



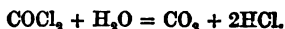
It may also be prepared from carbon tetrachloride by passing the vapour of that substance mixed with carbon dioxide over heated pumice—



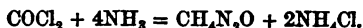
Carbonyl chloride may likewise be obtained by the oxidation of chloroform. 5 parts potassium dichromate, 40 parts strong sulphuric acid, and 2 parts of chloroform are gently heated in a flask in a water-bath. Carbonyl chloride, water, and free chlorine are simultaneously liberated. By passing the mixed gases over metallic antimony the chlorine is retained.

On cooling the purified gas to -15° it condenses to a limpid, mobile liquid of sp. gr. 1.432 at 0° . It boils at 8.2° , and gives off a vapour of an intensely suffocating odour. Carbonyl

chloride is gradually decomposed by water forming carbon dioxide and hydrochloric acid—



Treated with dry ammonia it forms *urea* and ammonium chloride—



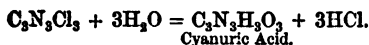
The existence of carbonyl bromide, COBr_2 , is not definitely established. It cannot be formed by the direct union of bromine and carbon monoxide in sunlight. The oxidation of bromoform has yielded no satisfactory results. Neither carbonyl iodide nor cyanide is known.

COMBINATIONS OF THE HALOGENS WITH CARBON AND NITROGEN.

Two polymeric cyanogen chlorides are known which at ordinary temperatures are respectively liquid and solid. The liquid modification has the formula CNCl ; the solid modification $\text{C}_2\text{N}_2\text{Cl}_2$.

190. Liquid Cyanogen Chloride, CyCl , is an excessively volatile and poisonous liquid, obtained by the action of chlorine upon moist mercuric cyanide, or by the action of chlorine upon prussic acid. It has an exceedingly repugnant odour, boils at 12.6° , and solidifies at -7° . When perfectly pure it may be kept unchanged for any length of time, but in presence of an excess of chlorine it is gradually converted into solid cyanogen chloride, Cy_2Cl_2 . It is miscible with water, alcohol, and ether, and is readily decomposed when heated with potassium, forming potassium cyanide and cyanate. With ammonia gas it forms ammonium chloride and *cyanamide*, CN_2H_2 .

191. Solid Cyanogen Chloride, Cy_2Cl_2 , may also be obtained by the action of dry chlorine upon heated potassium sulphocyanate. It is a white crystalline substance which melts at 140° , and boils at 190° . It is soluble in water; its aqueous solution is gradually resolved, especially on heating, into hydrochloric and *cyanuric* acids—

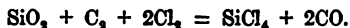


192. Cyanogen Bromide also occurs in two polymeric modifications. CNBr is best prepared by passing bromine vapour into a mixture of prussic acid and ether. It crystallizes in long needles, and is slightly volatile at ordinary temperatures; it has an exceedingly penetrating odour, and is highly poisonous. It is occasionally found in commercial bromine. When heated it is converted into Cy_3Br_3 (?), which melts above 300° .

193. Cyanogen Iodide, CyI , is occasionally formed in the manufacture of iodine. It has already been stated that it is sometimes found in commercial iodine. It may easily be obtained by heating iodine with cyanide of silver or mercury, or by adding iodine to a concentrated solution of potassium cyanide, and gently heating the solidified mass. Cyanogen iodide sublimes in long delicate needles, which, when recrystallized from alcohol, are transformed into small four-sided tables. It has an exceedingly pungent odour, and is very poisonous.

COMBINATIONS OF THE HALOGENS WITH SILICON.

194. Silicon Tetrachloride, SiCl_4 , unlike the corresponding carbon compound, may be formed by the direct union of its elements. Silicon readily burns when heated in chlorine gas. The compound is more easily obtained by mixing carbon and silica together into a stiff paste with oil, igniting the mixture in a covered crucible, and heating it in a stream of chlorine. Silicon tetrachloride is formed together with carbon monoxide—



Silicon tetrachloride is a clear, transparent liquid, of specific gravity 1.5237 at 0° . It boils at 59° , and does not solidify at -20° . It fumes strongly in a moist atmosphere, and is rapidly decomposed by water with formation of hydrochloric and silicic acids. When heated with potassium it forms silicon and potassium chloride.

195. Silicon Trichloride, Si_2Cl_6 (corresponding to carbon

trichloride, C_2Cl_6), is obtained by the action of carbon tetrachloride upon strongly heated silicon, or by gently heating the hexiodide (*vide infra*) with mercuric chloride. It is a colourless, mobile liquid, of specific gravity 1.58 at 0° . It solidifies at -14° (Troost and Hautefeuille); at -1° (Friedel), and boils at 147° . When strongly heated its vapour inflames spontaneously in the air, and when heated in sealed tubes under great pressure it is resolved into the tetrachloride and silicon. It is decomposed by alkaline solutions with the elimination of hydrogen.

Silicon dichloride is also believed to exist, but hitherto it has not been satisfactorily isolated.

A number of *silicon oxichlorides* have been obtained. Their formulæ and boiling points are given below (Troost and Hautefeuille)—

Si_2OCl_6	$136^\circ\text{--}138^\circ$.
$\text{Si}_2\text{O}_2\text{Cl}_8$	$198^\circ\text{--}202^\circ$.
$\text{Si}_2\text{O}_3\text{Cl}_{10}$	about 300° .
$\text{Si}_2\text{O}_4\text{Cl}_{12}$ (?).....	above 400° .
$\text{Si}_2\text{O}_5\text{Cl}_{14}$ (?).....	Solid at 440° .
$\text{Si}_2\text{O}_6\text{Cl}_{16}$	$152^\circ\text{--}154^\circ$.

196. Silicon Tetrabromide, SiBr_4 , may be obtained in the same manner as the chloride, by substituting bromine vapour for chlorine. It is a colourless, heavy liquid (specific gravity 2.813), which boils at 154° , and solidifies at 13° to a crystalline mass. It is decomposed by water and potassium in a similar manner to the chloride.

197. Silicon Tribromide, Si_2Br_6 , is formed by adding bromine to a solution of the tri-iodide in carbon bisulphide. It is a crystalline substance, and may be distilled at 240° without decomposition.

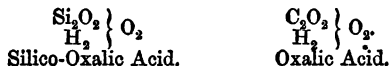
198. Silicon Tetriodide, SiI_4 , is formed by passing iodine vapour mixed with carbon dioxide over heated silicon. It crystallizes in transparent octahedrons, melts at 120.5° , and boils at about 300° , and may be distilled in a stream of carbon dioxide without decomposition.

199. Silicon Tri-iodide, Si_2I_6 , is obtained by heating the preceding compound with finely divided silver. It crystallizes in colourless hexagonal prisms, which fume in the air, and melt at about 250° . It is decomposed by potash solution

with formation of free hydrogen, silica, and hydriodic acid—



When treated with ice-cold water, it is converted into a white mass having the composition $\text{Si}_2\text{H}_2\text{O}_4$, analogous to oxalic acid—



200. Silicic Chloroform, SiHCl_3 , may be prepared by heating silicon in a stream of hydrochloric acid. It is an unstable liquid, which boils at 36° . Its vapour, mixed with air, inflames even in contact with a heated glass rod. It is decomposed by water with evolution of hydrogen, and by chlorine at ordinary temperatures with formation of silicon tetrachloride and hydrochloric acid—

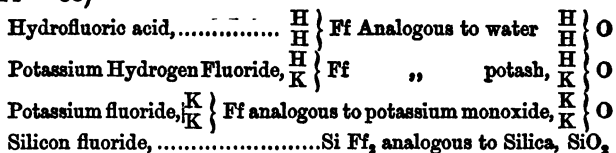


201. Silicic Iodoform, SiHI_3 , is obtained in small quantity by heating silicon in a stream of hydriodic acid and hydrogen. It is a transparent, highly refractive liquid of sp. gr. 3.362 at 0° . It boils at 220° , and is decomposed by water with formation of silica, hydriodic acid, and free hydrogen.

202. Fluorine—Symbol F; atomic weight 19.—This substance is very widely diffused in combination with calcium, forming fluorspar CaF_2 . It occurs also in certain minerals, *e.g.*, cryolite Na_3AlF_6 ; topaz $2\text{Al}_2\text{F}_7\text{SiF}_4 \cdot 5(\text{Al}_2\text{O}_3 \cdot \text{SiO}_2)$, fluorapatite $3\text{PO}_4\text{Ca}_3\text{CaF}_2$; wavellite, &c. Fluorine is an invariable constituent of bones, teeth, blood, and milk. It is found also in many ashes of plants and in river waters. The element itself has not yet been satisfactorily isolated. Silver fluoride is decomposed by iodine, and is said to yield a colourless gas of a smell resembling chlorine, which manifests an extraordinary power of combining with moisture to form hydrofluoric acid.

203. Hydrofluoric Acid, HF—Mol. weight 20; density 10.—This acid was discovered by Scheele in 1771, and may be made by heating potassium hydrogen fluoride, KFHF , to a

red heat in a platinum retort. It fumes strongly in the air, and can be condensed to a colourless, mobile liquid of sp. gr. 0.9879 at 12.8. It boils at 19.4°, and is exceedingly hygroscopic. If free from moisture, it exerts no corrosive action on glass. When dropped on the skin it forms painful wounds. The anhydrous acid is without action on the majority of metals. Potassium and sodium, however, eliminate hydrogen and form alkaline fluorides which unite with a second portion of the acid. It rapidly chars most organic substances, and explodes when mixed with oil of turpentine. The density of the acid shows that it is analogous in constitution to hydrochloric acid, 1 vol. of fluorine uniting with 1 vol. of hydrogen to form 2 vols. of hydrofluoric acid. It was at one time supposed that fluorine might be diatomic like oxygen, and that it would be found to possess the atomic weight 38, an idea which derived its chief support from the tendency of the elements to form double salts. According to this view the formula of the principal fluorides would be (Ff = 38)—



The vapour density of hydrofluoric acid, however, indicates that fluorine is analogous to chlorine, and that its atomic weight is 19.

The aqueous acid is now prepared on a comparatively large scale by heating a mixture of fluorspar and sulphuric acid in a leaden or platinum retort (fig. 94), $\text{CaF}_2 + \text{H}_2\text{SO}_4 = \text{CaSO}_4 + 2\text{HF}$. During the operation the U-shaped receiver is surrounded by a freezing mixture. The strongest acid which can be obtained in this way has a sp. gr. of 1.06. It combines with water with a hissing noise, and with great evolution of heat. The diluted acid containing 35.9 p. c. HF has a sp. gr. of 1.15. The aqueous acid rapidly attacks many metals. Copper and silver, which are not sensibly acted upon by hydrochloric acid, are readily dissolved by dilute hydrofluoric acid. Silver fluoride, unlike the chloride, is

soluble in water. The chief application of hydrofluoric acid depends upon its power of attacking silicates, due to the tendency of the fluorine to unite with silicon to form silicon tetrafluoride, $\text{SiO}_2 + 4\text{HF} = \text{SiF}_4 + 2\text{H}_2\text{O}$. The acid is accordingly used for etching on glass. The glass is coated

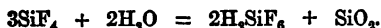


Fig. 94.

with wax, and the design is traced upon it by a sharp-pointed instrument; it is exposed to the acid either in the form of gas or in aqueous solution. The hydrofluoric acid rapidly attacks those portions which are left uncovered by the wax. The acid cannot therefore be preserved in glass bottles; it is generally kept in vessels of gutta percha, upon which it exerts no action. The only important salts of hydrofluoric acid are the fluorides of calcium and ammonium. The former substance is used as the source of the acid and as a flux, whence its name of *fluorspar* (from *fluo*, to flow). The latter is occasionally employed in analytical chemistry to expel silicon from its combinations; many silicates, when ignited with ammonium fluoride, part with the silicon in the form of silicon fluoride.

No oxygen, nitrogen, or carbon compound of fluorine is known.

204. Silicon Fluoride, SiF_4 , may be readily prepared by heating a mixture of fluorspar, sand, or powdered glass with strong sulphuric acid. It is a heavy, colourless, strongly fuming gas, which liquefies under pressure, and solidifies at -140° . It is absorbed by water, with formation of gelatinous silica and *silicofluoric acid*, H_2SiF_6 —



The gas is also absorbed by many metallic oxides, *e. g.*, lime which thereby becomes red hot. It combines with ammonia to form a crystalline compound, $2\text{NH}_3\text{SiF}_4$, which may be volatilized without change.

205. Silicofluoric or Hydrofluosilicic Acid, H_2SiF_6 , may

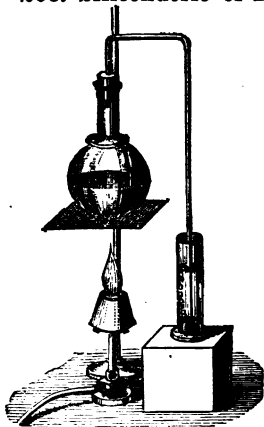


Fig. 95.

be prepared by means of the apparatus seen in fig. 95. Silicon fluoride, made in the manner above described, is evolved from the flask and is led into water, by which it is decomposed with the formation of silica and silicofluoric acid (*vide supra*). To prevent the delivery tube from being stopped up by the silica, the end dips beneath the surface of mercury. Each bubble of gas is decomposed on leaving the mercury, and the liquid quickly becomes gelatinous from the formation of silica. The solution of the acid is strained, filtered, and concentrated at a low temperature; it forms a fuming

liquid, which gradually attacks glass, especially on heating. Its salts are termed silicofluorides. They are generally soluble in water, and may be obtained well crystallized. The potassium compound, K_2SiF_6 , is one of the least soluble of the potassium salts. Silicofluoric acid is occasionally used as a test for that metal. Copper silicofluoride is one of the most soluble of copper salts, 1 part of water dissolving nearly 2 parts of the salt at ordinary temperatures.

CHAPTER XII.

THE SULPHUR GROUP.

This group comprises three members, *viz.*, sulphur, selenium, and tellurium, between which and oxygen exists a relation-

ship similar to that existing among the halogens. We notice the same gradation in the atomic weights of the members of the two groups—

Oxygen,.....16		Fluorine,.....19	
Sulphur,.....32		Chlorine,.....35·5	
Selenium,.....79·5	} mean 79·8.	Bromine,.....80	} mean 80·7.
Tellurium, ...128		Iodine,126·8	

The atomic weight of selenium is the mean of that of sulphur and tellurium, exactly as the atomic weight of bromine is midway between that of chlorine and iodine.

206. Sulphur—Symbol S; atomic weight 32; vapour density 32.

This substance has been known from the earliest times. Its ancient and familiar name of brimstone (from *brennestein*, the burning stone) denotes one of its chief characteristics, viz., its inflammability. It is not found in the free state in Great Britain; nearly all the native sulphur which finds its way into commerce comes from Sicily. It also occurs in Iceland, in various parts of Italy, in Mexico, South America, &c.; indeed, free sulphur is invariably found in more or less quantity in all volcanic districts. In a state of combination, sulphur occurs associated with iron and copper, forming pyrites; with zinc it forms zinc blende; with lead, galena; with mercury, cinnabar, &c.; in fact, the sulphides constitute some of the most valuable metalliferous ores.

Combined with oxygen and bases, sulphur occurs as gypsum and selenite (calcium sulphate), as heavy spar (barium sulphate), as celestine (strontium sulphate), as Epsom salts (magnesium sulphate), &c. Sulphur is also found associated with hydrogen as sulphuretted hydrogen, and with carbon and oxygen as carbon oxysulphide in many mineral waters. The hepatic waters of Harrogate and Aix la Chapelle owe their medicinal value to the sulphur which they hold in solution. Sulphur is likewise found in the unoxidized condition in vegetable and animal tissues, in albumen, in the taurin of bile, and in the cystin in urine. Many volatile oils, —e. g., oil of mustard, oil of garlic—contain sulphur derivatives, which confer upon them characteristic alliaceous odours.

The exportation of sulphur constitutes one of the staple industries of Sicily. The deposition of the sulphur in volcanic

regions has probably been brought about by the action of sulphuretted hydrogen, steam, and air upon chalk. Bischof has shown that when these gases are passed over calcium carbonate heated to 100° , gypsum is formed and sulphur is deposited. This explanation of the origin of the sulphur deposits derives some support from the fact that chalk and gypsum are almost invariably associated with the sulphur, and that sulphuretted hydrogen, accompanied by jets of steam and finely divided sulphur, is largely evolved from all parts in the district.

207. Extraction of Sulphur.—When quarried, the sulphur

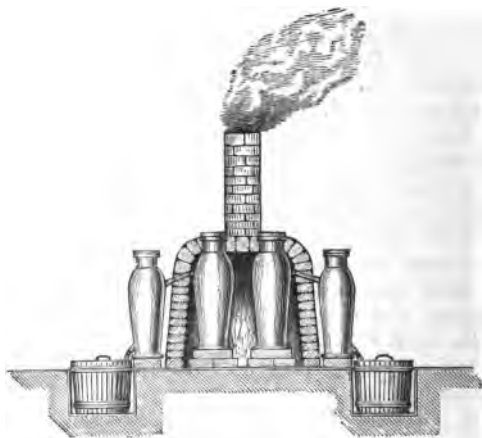


Fig. 96.

is always associated with earthy matter. The richer portions are melted in an iron pot, and the sulphur is ladled out into cold water, in which it congeals. The residue still contains sulphur, which is extracted by distillation. This latter process is always used for the poorer deposits, *i. e.*, for those containing from 8 to 12 per cent. of sulphur. The sulphur ore is placed in earthenware pots ranged in a furnace, and connected with similar pots which act as condensers; the molten sulphur flows out through the lower openings of the receivers into tubs filled with cold water, where it solidifies (fig. 96).

The *rough sulphur*, as the product of this operation is termed, is purified by a second distillation, conducted in the arrangement seen in fig. 97. The crude sulphur is melted in the iron pot *a*, and run off by the pipe *b* into the iron retort *c*, and it is caused to boil by the fire at *d*; the vapours are led into the large chamber *eee*, which has a capacity of about 7,000 cubic feet, and is constructed of thick brickwork. By means of the valve *s*, the draught into the chamber may be duly regulated. The sulphur vapour for some time after the

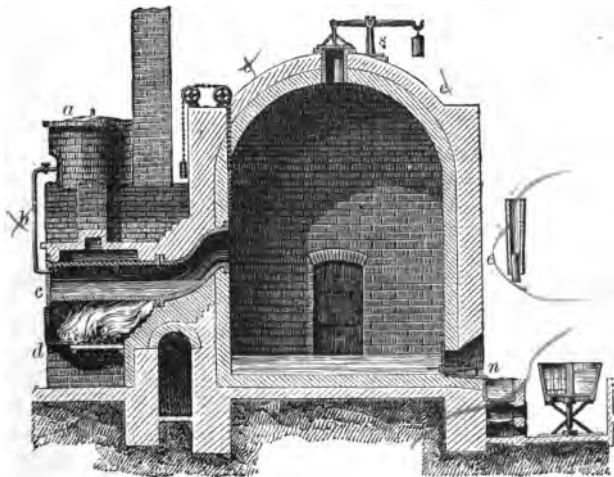


Fig. 97.

commencement of the operation condenses upon the walls in the form of microscopic crystals, termed *flowers of sulphur*. As the brickwork becomes heated, the molten sulphur flows down and accumulates at the bottom, whence it is drawn off by the aperture *n*, and cast into wooden moulds, constituting *roll sulphur*. Occasionally it is allowed to congeal at the bottom, when it forms refined lump sulphur.

Sulphur in an exceedingly finely divided state is employed in medicine under the name of *milk of sulphur*. This preparation is made by boiling flowers of sulphur with milk of

lime, or with an alkali. On adding hydrochloric acid to the clear solution of the alkaline sulphide, sulphur is precipitated as a light greenish-yellow, amorphous powder.

Large quantities of combined sulphur exist in Great Britain and Ireland as iron and copper pyrites. These substances, when heated, part with a portion of their sulphur, and if care is taken to regulate the supply of air, a certain proportion of the sulphur may be obtained in the unoxidized state. A quantity of brushwood is spread over the ground, or on a layer of broken pyrites, and a huge heap of the ore, containing about 2,000 tons, is placed over it, a central space or flue leading to the brushwood being left in the pile. The wood is set on fire by throwing lighted faggots down the centre space, and as the mass of ore is thus gradually heated, the sulphur trickles down, and is collected in cavities in the walls of the heap. The operation of burning such a heap lasts about six months, and the pyrites yield about 1 per cent. of crude sulphur. The sulphur is in reality only obtained as a bye product, the burning being simply a preliminary stage in the extraction of the more valuable copper.

It has been already mentioned that oxide of iron is often used to abstract the sulphur compounds from coal gas. If the moist ferrous sulphide formed in the purifier is exposed to air it is gradually reconverted into ferric hydrate and sulphur, and it is fitted to absorb a further quantity of sulphuretted hydrogen from the gas. The mass is alternately exposed to the action of the coal gas and to air, until the sulphur amounts to 40 or 50 per cent., when it is distilled off in iron retorts.

For the methods of extracting sulphur from *alkali waste*, see *Manufacture of Sodium Carbonate*, vol. II.

208. Properties of Sulphur.—Sulphur is a brittle solid, of a lemon-yellow colour; it is insoluble in water, and possesses little odour. It is an exceedingly bad conductor of heat and of electricity. If a roll of sulphur be warmed in the hand it emits a crackling sound, and ultimately breaks in pieces from the irregular manner in which it is heated. It becomes negatively electric when rubbed with hair or wool. Native sulphur melts at 115° to a limpid, amber-coloured liquid, which solidifies on cooling to a transparent vitreous mass, provided it has not been heated above 120° . The

action of heat upon sulphur is very remarkable. When heated above 120° the limpid, orange coloured liquid gradually darkens in colour, and becomes viscid; at 200° — 250° the mass is almost black, and so viscid that the flask in which it is contained may be inverted without the sulphur flowing out. On continuing the heat the dark coloured substance becomes more and more mobile, until its boiling point, viz., 440° is reached, when it is transformed into an orange-coloured gas; its mobility, however, is never so great as when it is first melted. On allowing the sulphur to cool it passes inversely through the same series of changes. Sulphur vapour exists only in the state of a true gas at about 1000° . The density of its vapour is only normal—that is, 32 times greater than that of hydrogen when measured at that temperature; at 500° its vapour density is thrice the calculated quantity.

Sulphur occurs in at least three allotropic modifications, distinguished by differences in crystalline form and in solubility in carbon bisulphide. Native sulphur is found in large octahedral crystals belonging to the rhombic system. This modification has a sp. gr. of 2.05, and is readily soluble in carbon bisulphide, benzene, oil of turpentine, heavy petroleum oils, &c. Carbon bisulphide dissolves one-third of its weight of sulphur at ordinary temperatures, and at about 40° it dissolves its own weight. On allowing the solvent to evaporate the sulphur crystallizes in well defined octahedrons. Sulphur may be crystallized in this form by fusion. A long necked flask is filled with sulphur, which is melted by immersing the flask in an oil bath heated to 120° . If the vessel be slowly cooled by plunging it into water at 90° , crystals are seen to form in the liquid, and may be isolated by suddenly inverting the flask and allowing the non-solidified portion to flow into the neck. The crystals thus obtained are permanent, and are identical with those of natural sulphur.

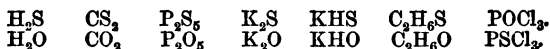
If a quantity of sulphur be melted in a crucible and allowed to cool quickly, and the superficial crust be broken, and the still liquid portion poured out, on breaking the crucible its walls will be found to be lined with transparent waxy-looking needles, which belong to the monoclinic system. Sulphur accordingly is dimorphous. The needle shaped modification melts at 120° , and has a sp. gr. of 1.98. It

tends to pass into the octahedral form. If the crystals are scratched, they gradually become opaque, and crumble to a powder consisting of minute octahedrons. Sulphur is occasionally deposited from a hot saturated solution in oil of turpentine or petroleum in the needle shaped or prismatic form. The crystals which are deposited as the solution cools belong to the rhombic or naturally occurring form. When originally cast in rolls the sulphur is in the prismatic form, but in process of time it changes into the octahedral variety. Its condition is now like that of unannealed glass; it is exceedingly brittle, and readily breaks on heating.

If melted sulphur, heated to about 280° , be poured into cold water it does not immediately congeal. Even when quite cold it forms a soft, tenacious mass, like semi-molten caoutchouc, which may be drawn out into long threads. This *plastic modification* of sulphur has a sp. gr. of 1.95, and is insoluble in carbon bisulphide. It may be obtained perfectly solid by cooling it in a mixture of solid carbon dioxide and ether, but at ordinary temperatures it reassumes the plastic condition. In time, however, it loses its transparency, and passes into the octahedral variety with evolution of heat.

Sulphur is a very active chemical element. Hydrogen passed through molten sulphur combines with it, forming sulphuretted hydrogen. With oxygen it forms two compounds, termed sulphur dioxide SO_2 , and sulphur trioxide SO_3 . The first named compound is formed when sulphur burns in the air. With carbon at a red heat it forms carbon bisulphide. Many metals combine directly with sulphur. If copper be gently heated in sulphur vapour, combination occurs with the evolution of great heat, and the metal glows with a bright red light.

Sulphur is the analogue of oxygen, a marked similarity existing both in the constitution and mode of formation of sulphur and oxygen compounds—



It is evident from these formulæ that sulphur is chemically equivalent to oxygen, one atom of which, as we have before seen, is equal to two atoms of hydrogen or chlorine. In fact,

we can obtain sulphur compounds the composition of which indicates that one atom of sulphur replaces two of chlorine. Thus, carbon monoxide and sulphur unite directly together to form carbon oxysulphide, COS , exactly in the same manner that carbon monoxide and chlorine generate phosgene gas, COCl_2 .

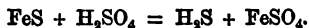
COMBINATIONS OF SULPHUR AND HYDROGEN.

The parallelism between oxygen and sulphur is exhibited in the sulphides of hydrogen, of which there are two, corresponding to the oxides of hydrogen,* viz. :—

Sulphuretted Hydrogen, or	{ H_2S .	Water, or Hydrogen	{ H_2O .
Hydrogen Monosulphide,		Monoxide,	
Hydrogen Persulphide, H_2S_2 (?)		Hydrogen Dioxide, H_2O_2 .	

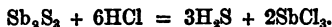
209. Sulphuretted Hydrogen (*Sulphydric or Hydrosulphuric Acid*)—Symbol H_2S ; molecular weight 34; density 17.—This gas may be formed, as we have already stated, by passing a current of hydrogen through boiling sulphur. A jet of hydrogen, when lighted and plunged into an atmosphere of sulphur vapour, continues to burn with formation of sulphuretted hydrogen; this substance may also be formed by burning sulphur vapour in hydrogen, exactly as water is produced by burning hydrogen in oxygen or oxygen in hydrogen. This gas is contained in many volcanic exhalations, and it is evolved in the decay of organic substances containing sulphur. Decomposing organic matter, in contact with aqueous solutions of sulphates, frequently generates sulphuretted hydrogen. From this cause sulphides are occasionally found in sea water at the mouths of large rivers, which bring down quantities of decaying organic matter.

210. Its Preparation and Properties.—In the laboratory sulphuretted hydrogen is made by treating ferrous sulphide with sulphuric acid, ferrous sulphate being simultaneously formed—



* The composition of the persulphide is still a matter of dispute. Hofmann has adduced evidence to show that it has the formula H_2S_2 (*vide infra*).

A purer product may be obtained by heating antimony tersulphide with hydrochloric acid—



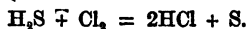
Sulphuretted hydrogen is a colourless gas of an offensive odour, resembling that of rotten eggs, the smell of which is, in fact, due to the formation of this gas from the decomposition of the protein or sulphur compounds contained in the albumen. The discoloration which a silver spoon suffers by contact with an egg arises from the formation of a thin film of silver sulphide. Sulphuretted hydrogen is a poisonous gas when breathed in quantity; even when considerably diluted with air it occasions headache and sickness. It is readily inflammable, and burns with a light-blue flame, forming sulphur dioxide and water when the supply of air is abundant; when deficient, water is mainly produced and sulphur is deposited. By the application of great cold and pressure the gas may be condensed to a thin, mobile liquid of specific gravity 0.9, which may be frozen to a white, transparent mass, melting at -85° .

Sulphuretted hydrogen gas is decomposed when heated with certain metals—*e. g.*, cadmium and tin, with liberation of hydrogen and formation of metallic sulphides—



The volume of hydrogen left after the decomposition is found to be equivalent to that of the sulphuretted hydrogen originally taken—showing that this gas is made up of two volumes of hydrogen, and one volume of sulphur vapour condensed to two volumes.

The gas is instantly decomposed by chlorine with formation of hydrochloric acid and deposition of sulphur—



Sulphuretted hydrogen is soluble in water, which absorbs about three times its volume of the gas, and thereby acquires its disgusting odour and taste. This solution gives with certain metallic solutions characteristic precipitates which may be used as tests for the metals. Thus, with cadmium salts sulphuretted hydrogen gives a bright yellow precipitate of cadmium sulphide, soluble in hot hydrochloric acid, and readily

soluble in nitric and sulphuric acids; with antimony sulphuretted hydrogen occasions an orange precipitate of antimony tersulphide, Sb_2S_3 ; with arsenic a yellow precipitate of As_2S_3 ; with tin a brown or black precipitate of tin sulphide; copper lead, bismuth and mercury give black precipitates of their respective sulphides with sulphuretted hydrogen.

If a current of sulphuretted hydrogen gas be passed into a solution of potassium, ammonium, or barium hydroxide, a soluble sulphhydrate or sulphide is formed. Thus, in the case of barium we obtain BaS or BaH_2S_2 , corresponding to barium monoxide BaO , or barium hydrate BaH_2O_2 .

If a solution of an alkaline sulphide or sulphhydrate be added to any of the salts of the heavy metals, insoluble sulphides are formed. Thus, with copper salts we obtain cuprous sulphide; with iron salts, black ferrous sulphide; with zinc, white zinc sulphide, &c. Certain of the metallic sulphides, *e. g.*, those of iron, zinc, cobalt, nickel, &c., are most readily obtained in the wet way by the addition of an alkaline sulphide. A few of the metallic sulphides, *e. g.*, those of arsenic, antimony, and tin, are soluble in excess of the solutions of the alkaline sulphides. On the different behaviour of the metals towards sulphuretted hydrogen and a solution of an alkaline sulphide, is based a method of subdividing the metals into groups, which is of great service in analytical chemistry.

211. Hydrogen Persulphide — Symbol H_2S_2 (?); or H_2S_3 (?).—This compound, which bears a marked analogy in its chemical deportment to hydrogen dioxide, is made by adding a persulphide of an alkali, or alkaline earth, to dilute hydrochloric acid—



Hydrogen persulphide is a heavy, yellow oil of a characteristic sulphurous smell. It is very unstable, and is gradually decomposed on keeping into sulphuretted hydrogen and free sulphur. At a slightly elevated temperature this decomposition is very rapid. If a quantity of the persulphide be heated in one limb of a sealed V tube, the sulphuretted hydrogen which is liberated is condensed to a liquid by its own pressure. Hydrogen persulphide is insoluble in water, but

readily dissolves in ether. It is inflammable, and burns with a blue flame. Hydrogen persulphide, like the dioxide, is decomposed by many metallic oxides, or finely divided metals. The composition of this remarkable substance is not conclusively determined, as it readily dissolves sulphur, from which it cannot be separated without decomposition.

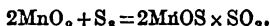
Hydrogen persulphide appears to combine with many vegeto-alkaloids. If a strong solution of strychnine in alcohol be mixed with an alcoholic solution of ammonium sulphide containing free sulphur, orange-red crystals of the composition $C_{24}H_{22}N_2O_2 \cdot H_2S_2$ separate out. This substance is decomposed by sulphuric acid, with formation of strychnine sulphate and precipitation of the hydrogen persulphide in oily drops. The persulphide would thus appear to have the formula H_2S_2 , and not that of H_2S_3 , corresponding to hydrogen dioxide—(Hofmann).

COMBINATIONS OF SULPHUR WITH OXYGEN AND HYDROGEN.

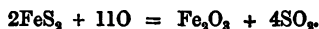
Two oxides of sulphur are known, viz., sulphur dioxide SO_2 , and sulphur trioxide SO_3 . The former compound is formed by burning sulphur in oxygen or in air. Sulphur trioxide may be produced by the indirect oxidation of the dioxide. However large the supply of oxygen may be, it is never formed by the direct union of oxygen and sulphur. These oxides of sulphur produce corresponding acids, termed respectively sulphurous and sulphuric acids. In addition, we have a complete series of acids, the anhydrides of which have not yet been discovered. The names and formulæ of the acids are given below—

Acid.	Anhydrida.
Hyposulphurous Acid, H_2SO_2 ,	—
Sulphurous Acid, H_2SO_3 ,	SO_2
Sulphuric Acid, H_2SO_4 ,	SO_3
Thiosulphuric Acid (commonly called Hyposulphurous Acid), $H_2S_2O_3$,	—
Polythionic Acids, {	Dithionic Acid, $H_2S_2O_6$, —
	Trithionic Acid, $H_2S_3O_6$, —
	Tetrathionic Acid, $H_2S_4O_6$, —
	Pentathionic Acid, $H_2S_5O_6$, —

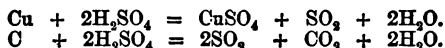
212. Sulphur Dioxide.—Symbol SO_2 ; mol. weight 64; density 32.—This substance may be formed by heating sulphur with oxygen or with many metallic peroxides. With manganese dioxide, for example, manganese oxysulphide and sulphur dioxide are formed—



Many metallic sulphides—*e. g.*, iron pyrites, FeS_2 —when roasted in air produce sulphur dioxide, and are converted into oxides—



This gas may also be obtained by deoxidizing sulphuric acid by means of charcoal or copper—



In the laboratory the former reaction is generally made use of. The copper, in clippings or borings, is placed in a flask and covered with strong oil of vitriol. On heating, the gas is abundantly disengaged, and may be washed from any accompanying vapours of sulphuric acid by passing through water. In the case of copper the reaction is not quite so simple as would appear from the preceding equation. The residue in the flask always contains cuprous and cupric sulphides, produced in all probability by the reducing action of the sulphur dioxide upon the copper sulphate formed.

Sulphur dioxide may also be formed by heating a mixture of dehydrated ferrous sulphate with sulphur—



The residual ferrous sulphide may be used for the preparation of sulphuretted hydrogen.

Sulphur dioxide, at ordinary temperatures, is a colourless, incombustible, irrespirable gas, possessing the odour of burning sulphur. It is one of the most easily liquefiable of the gases; by exposure to a pressure of three atmospheres at common temperatures, or by cooling the gas to -18° by a mixture of snow and salt (fig. 98), it condenses to a thin mobile liquid of specific gravity 1.45, which boils at -10° . By cooling the liquid in a mixture of solid carbon dioxide and

ether it solidifies to a transparent mass, heavier than the liquid, which melts at -79° . Liquid sulphur dioxide dissolves phosphorus, sulphur, iodine, and many resins, and mixes unchanged with carbon bisulphide, ether, benzol, chloroform, bromine, &c. Sulphuric and phosphoric acids are not dissolved by it.

Sulphur dioxide gas is readily soluble in water, which at 10° takes up about 51 volumes, and at 20° , 36 volumes, and forms a solution of the true sulphurous acid, H_2SO_3 .

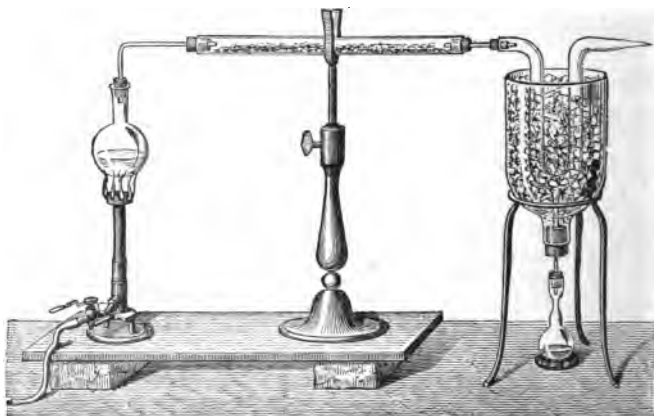


Fig. 98.

On strongly cooling the liquid, a crystalline hydrate, having the formula $\text{H}_2\text{SO}_3 \cdot 8\text{H}_2\text{O}$, and fusing at 4° , is obtained. The solution possesses the characteristic odour of the gas; on heating it sulphur dioxide is evolved, although prolonged ebullition is required to expel the last traces of the gas. The liquid has a strong acid reaction, and when added to a carbonate it expels carbon dioxide. On exposure to the air it gradually oxidizes to sulphuric acid. Nascent hydrogen converts it into sulphuretted hydrogen; if treated with zinc and hydrochloric acid, the issuing hydrogen will blacken a strip of lead paper from the formation of lead sulphide. If treated with zinc alone the sulphurous acid is converted into hyposulphurous acid,

H_2SO_2 . Both the oxide and the acid act as strong reducing agents. Very small quantities of sulphur dioxide may be detected by its power of reducing iodic acid to iodine. If a piece of paper coated with a mixture of starch paste and iodic acid be exposed to the gas, the reduced iodine will colour the starch intensely blue. If the amount of sulphur dioxide be large, the moist iodide of starch will be gradually bleached, owing to the decomposition of water, the oxygen converting the sulphurous acid into sulphuric acid, and the hydrogen combining with the iodine to form hydriodic acid, which is without action on starch. An acidulated solution of potassium permanganate is instantly decolorized by the gas or its solution. In the arts, sulphur dioxide is used to bleach woollen and silk goods, isinglass, sponges, straw, &c. It will be noticed that in all these bleaching actions sulphur dioxide acts in a manner diametrically opposite to that of chlorine; the one decolorizes by reduction, the other by oxidation. Sulphur dioxide is used to some extent as an *antichlor*, from its power of decomposing water in presence of chlorine; fabrics bleached by chlorine are occasionally dipped in a solution of sulphurous oxide to remove the last traces of the halogen—



Sulphur dioxide is also used as a disinfectant. The wards of fever hospitals and the clothes of fever patients are sometimes purified by treatment with the fumes of burning sulphur. A solution of sulphurous acid or a sulphite is occasionally employed to stop acetous fermentation. Vegetable and fruit extracts, *e. g.*, lime juice, are often "cured" by the so-called "bisulphite of lime" solution.

Sulphurous acid is dibasic, forming acid and normal salts. The salts are usually prepared by passing the oxide into water in which the hydrated base or its carbonate is suspended or dissolved. The soluble salts are crystalline, and when solid are stable. In aqueous solution they gradually become oxidized to sulphates.

213. Sulphur Trioxide or Sulphuric Anhydride.—Symbol

SO_3 ; molecular weight 80.—This remarkable substance may be prepared by the direct oxidation of sulphur dioxide under the influence of finely divided platinum. A stream of oxygen from the gasometer (fig. 99) is passed through a strong aqueous solution of sulphur dioxide; the mixed gases,

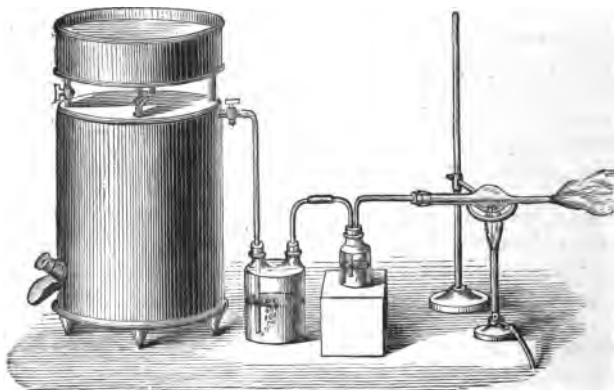
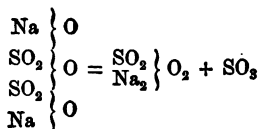


Fig. 99.

when heated in contact with the platinized asbestos in the bulbed tube combine, and dense fumes of sulphur dioxide make their appearance at the exit tube of the apparatus. Sulphur trioxide may also be obtained by heating dehydrated acid sodium sulphate to low redness—



Dehydrated ferrous sulphate, when similarly treated, yields ferric oxide and a combination of sulphuric acid and sulphur trioxide, known as Nordhausen oil of vitriol, from the name of the place in Saxony where the manufacture is carried on. This substance is used in the arts as a solvent for indigo. Its

composition and relation to the dehydrated acid sodium sulphate are exhibited by the following formulæ:—



Nordhausen Sulphuric Acid.

When the Nordhausen acid is gently heated it parts with the trioxide, which may be condensed in a well cooled receiver.

Sulphur trioxide may also be obtained by heating ordinary oil of vitriol with phosphorus pentoxide. Sulphur trioxide at ordinary temperature forms long fibrous crystals of a beautiful silky lustre. The substance is extremely volatile. Its sp. gr. is 1.9456 at 13°* (Morveau); it melts at 16°, and boils at 46° (Schultz-Sellack).

The liquid sulphur trioxide expands in a remarkable manner on heating. Between 25° and 45° its mean expansion-coefficient amounts to 0.0017 for 1°—i. e., more than $\frac{1}{2}$ of that of the gases. When perfectly dry, solid sulphur trioxide may be handled with impunity, but it quickly absorbs water from the air, and then exerts a powerful corrosive action. When free from moisture, it has no action on litmus. Its vapour is resolved into sulphur dioxide and oxygen when passed through a red-hot tube. In contact with barium or calcium monoxide heated to low redness, barium or calcium sulphate is formed with vivid incandescence. Sulphur trioxide dissolves sulphur, forming liquids which are variously coloured—brown, green, and blue—according to the proportion of the sulphur which they contain. The trioxide unites with iodine, producing a green crystalline compound, and absorbs nitrogen tetroxide, forming a white fusible crystalline mass having the composition NO_2SO_3 . When this substance is strongly heated it parts with oxygen, and is converted into a crystalline compound, $\text{N}_2\text{O}_5\text{SO}_3$. This body may be regarded as Nordhausen oil of vitriol, in

* The sp. gr. of the liquid trioxide is stated by Bussy to be 1.97 at 20°. There is probably some mistake in one or other of these statements.

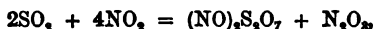
which the atoms of hydrogen are replaced by an equivalent quantity of azotyl—



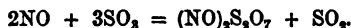
Nordhausen Acid.

Azotyl Anhydrosulphate.

The same compound may also be obtained by passing nitrogen tetroxide vapour into liquid sulphur dioxide—

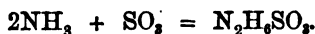
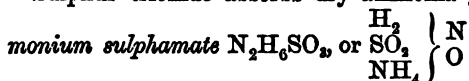


or by passing nitrogen dioxide over sulphur trioxide—



It may also be formed directly by the action of induction sparks upon a mixture of sulphur dioxide, oxygen, and nitrogen, or by passing sulphur dioxide over strongly heated lead nitrate.

Sulphur trioxide absorbs dry ammonia gas, forming *am-*



This substance is a white crystalline powder, permanent in the air, and soluble in water, from which it crystallizes unchanged.

214. Sulphuric Acid— H_2SO_4 , or $\text{SO}_2 \left\{ \begin{array}{c} \text{H}_2 \\ \text{H}_2 \end{array} \right\} \text{O}_2$, molecular weight 98.—This, the most important of all the acids, may be obtained by the addition of water to sulphur trioxide. This substance in contact with water hisses like a red-hot iron from the energy of the combination. Sulphuric acid is also formed, as we have stated, by the gradual oxidation of sulphurous acid in aqueous solution. Accordingly sulphuric acid is not unfrequently met with in the free state in the waters emanating from volcanic districts. The discovery of sulphuric acid is generally attributed to Basil Valentine, but

in all probability it has been known since the ninth century; the first correct description of its properties appears to have been given by an alchemist named Dorneas, in 1590.

The acid was originally entirely made by heating dried ferrous sulphate or green vitriol, whence its familiar name of oil of vitriol. This process is still carried on, among other places, at Nordhausen in Saxony, and at Radnitz in Bohemia.

The distillation is effected in the following manner:—A number of cylindrical earthenware retorts, filled with the dehydrated green vitriol, are arranged horizontally in a furnace, and connected with earthenware receivers. At a bright red heat dense white vapours of sulphur trioxide and sulphuric acid pass over into the receivers, and reddish brown ferric oxide remains in the retorts. This oxide is used to some extent as a pigment, and is known under the name of *colcothar*. A more economical process consisted in deflagrating a mixture of nitre and sulphur in large glass jars, condensing the fumes in water, and concentrating the liquid by

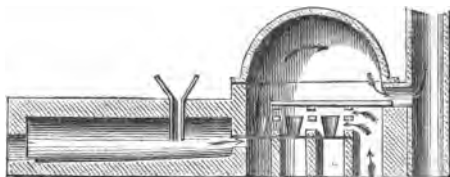


Fig. 100.

boiling in retorts. Dr. Roebuck of Birmingham, in 1786, substituted leaden vessels for glass, and thereby laid the foundation of the present method of manufacturing this acid. Immense quantities of sulphuric acid are now made in this country; in South Lancashire alone more than 3000 tons are weekly produced. The principle of the method at present used is identical with that employed by Roebuck. Sulphur dioxide produced from burning sulphur or by the combustion of pyrites is led into a large leaden chamber and is mixed

with nitroxygen fumes and steam, and the acid liquid thus obtained is concentrated by boiling.

Fig. 100 shows the arrangement of a furnace much used for the combustion of sulphur. The sulphur is introduced through the "hopper" on to the bed of the furnace, and by the due admission of air through holes in the door, it is partially oxidized to sulphur dioxide, partly vaporized uncombined. The mixed vapours pass into the "combustion oven," where they meet with a fresh supply of air, admitted by a side aperture, and are thus completely oxidized. The sulphur dioxide traverses the flues in the direction indicated by the arrows, and passes over the nitre pots containing a mixture of Chili saltpetre and sulphuric acid. The nitrogen fumes and sulphur dioxide mix in the dome, and pass thence into the leaden chamber, where the reaction is completed.

Fig. 101 shows one of the many forms of furnaces which have been proposed for roasting the pyrites. From $3\frac{1}{2}$ to 4 cwts.

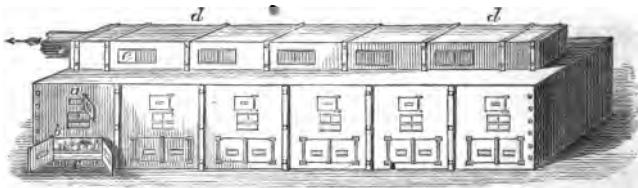


Fig. 101.

of "lump" sulphur ore is thrown into the furnace every twelve hours through the opening *a*, which can be closed by a sliding door, in which there is a small slit for the admission of air and for watching the progress of the operation. From time to time the mass of burning ore is stirred by a poker introduced at *b* (which can also be closed by a sliding door), to prevent it fusing together, and to bring fresh surfaces in free contact with air; when exhausted the ore, which now mainly consists of ferric oxide, is raked out through the openings *c*. The sulphur dioxide passes into the flue leading to the lead chamber; in this flue are placed the nitre pots introduced through the openings *e*, which can be closed by sliding doors. The general composition of the pyrites employed may be thus represented—

Sulphur.	Iron.	Lead.	Copper.	Arsenic.	Silica, &c.	
45.21	43.50	0.22	2.21	0.41	8.31	= 99.86.

In general about 3 per cent. of the sulphur remains unburnt in the ore. If the pyrites is associated with calcium carbonate, the quantity of sulphur thus retained is considerably increased.

The complete expulsion of the sulphur requires a high temperature. The first action of heat in presence of air effects the removal of a moiety only of the sulphur, the remainder, *i. e.*, that existing as ferrous sulphide, being eliminated on increasing the temperature. Occasionally the gases are cooled before entering the chamber by passing through a pipe surrounded by cold water. This preliminary cooling allows of the deposition of the main quantity of the arsenic trioxide derived from the pyrites.

The chamber in which the gases react upon one another is made of thin sheet lead, supported by a wooden framework. The sheets of lead are fastened to the woodwork by straps of the metal soldered to the sheets, which are cemented together by *autogenous* soldering, an oxyhydrogen flame being directed against the edges of the sheets until they are fused together. The bottom of the chamber is simply an immense leaden cistern, from 12 to 18 inches in depth, into which the sides of the chamber fit in the manner represented in fig. 103. The floor sometimes rests directly on the ground, but more frequently the chamber is supported on stone or brick pillars, the space underneath being occupied by the pyrites burners, or by the retorts employed to concentrate the acid. The size of the chambers is exceedingly variable; some manufacturers prefer to use very large chambers, others employ smaller ones, and work them in sets. Fig. 102 represents the arrangement employed to draw off the acid. The side of the chamber is fitted with a recess, the end of which dips below the level of the acid on the floor. The shorter limb of the syphon, which is always maintained full of liquid, ends near the floor; the other end dips into the vessel, which is thus always filled with the acid. The liquid

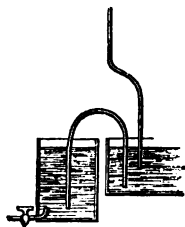


Fig. 102.

is drawn off by the pipe furnished with a stopcock; its end turns up within the tank, in order that the acid may be drawn off without sediment. Fig.

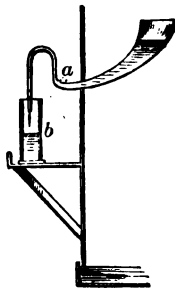
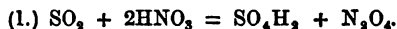


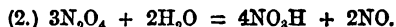
Fig. 103.

103 represents the arrangement, termed the drip pipe, by which the manufacturer ascertains the progress of the operations within the chamber. It consists of a leaden pipe, *a*, fitted into the side of the chamber, and terminating within it in a funnel-shaped aperture. The portion of the pipe on the outside of the chamber is bent in the form of a syphon, and dips into a cylindrical vessel, *b*, standing on a shelf. The arrangement acts precisely like a rain gauge; the condensed acid falls into the funnel, fills the pipe, and flows over into the vessel *b*, where the rapidity of its formation and its strength are determined.*

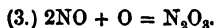
The theory of the manufacture of sulphuric acid is still incompletely understood. The reaction which goes on in the leaden chamber may be thus generally stated:—In the first place, the sulphur dioxide and nitric acid react upon each other to form sulphuric acid and nitrogen tetroxide—



In presence of steam the tetroxide is resolved into nitric acid and nitrogen dioxide—



The nitric acid is again reduced by sulphur dioxide in accordance with equation (1.), whilst the nitrogen dioxide in contact with atmospheric air takes up an atom of oxygen, and is converted into nitrogen trioxide—



Nitrogen trioxide, in contact with sulphur dioxide and steam, is immediately converted into sulphuric acid and nitrogen dioxide, which again takes up oxygen and transfers

* For a description of Sprengel's apparatus for gauging the depth of acid on the floor of the chamber, see *Chem. Soc. Jour.* [2], iv. 455.

it to a second molecule of sulphur dioxide; a small quantity of nitric acid vapour being thus theoretically able, in presence of steam and atmospheric air, to convert an indefinitely large quantity of sulphur dioxide into sulphuric acid—



The primary action of the sulphur dioxide upon the nitric acid has been otherwise stated. The mutual action of the two substances results in the formation of a white crystalline compound of the composition $\text{SO}_2 \begin{cases} \text{NO}_2 \\ \text{OH} \end{cases}$, which is decomposed by the steam into sulphuric and nitrous acids. The last named substance is quickly resolved into nitric acid and nitrogen dioxide (see p. 202), and thus brings about the oxidation of fresh portions of sulphur dioxide. The formation of these white crystals (the so-called chamber crystals) is thus supposed to play an important part in the manufacture of the acid. The mutual action of the

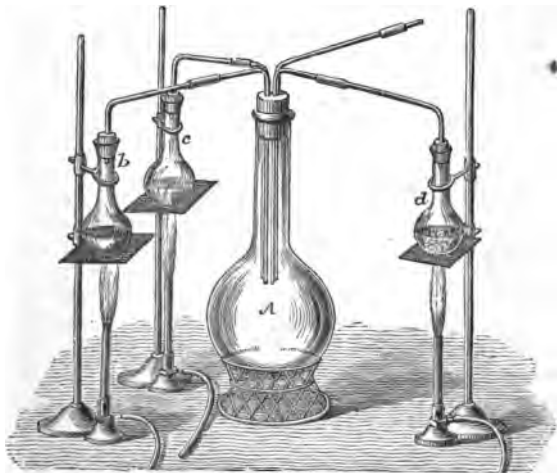


Fig. 104.

sulphur dioxide, nitroxygen fumes, and steam may be illustrated by means of the apparatus seen in fig. 104. The glass globe A, representing the leaden chamber, is filled with

red fumes, by sending into it a quantity of nitrogen dioxide evolved from nitric acid and copper contained in the flask *b*. Flask *b* is removed, and flask *c*, containing copper and oil of vitriol, is heated, and the evolved sulphur dioxide is delivered into *A*. The sulphur dioxide and nitroxygen fumes act upon each other, and a thin crystalline crust forms upon the surface of the glass. If steam be now driven into the chamber from the flask *d*, the white substance will be decomposed, and the atmosphere within the globe will be rendered completely colourless. On blowing air into *A*, red fumes will again make their appearance, and these will again be destroyed in contact with fresh sulphur dioxide. The acid liquid at the bottom of *A* will give all the reactions for sulphuric acid.

Whatever may be the exact nature of the reaction, it is evident that it requires the use of large chambers—(1.) Because to obtain any considerable weight of acid it is necessary to operate upon large volumes of gases; and (2.) Since the air contains only one-fifth by volume of oxygen the gases become diluted with a large bulk of nitrogen, derived partly from the pyrites burners, and partly from that admitted to oxidize the nitrogen compounds. Although, theoretically speaking, a small quantity of nitric acid or nitrogen dioxide should convert an indefinitely large quantity of sulphur dioxide in presence of water and air into sulphuric acid, yet in practice it is found necessary to continually send into the chamber fresh quantities of nitroxygen fumes. The dilute sulphuric acid absorbs a certain proportion of these gases, whilst a second portion is swept out of the chamber along with the escaping nitrogen. Formerly the waste nitrous fumes were allowed to escape directly into the air, but in many works they are retained and re-utilized according to the plan proposed by Gay Lussac. This consists in absorbing the vapours at the exit end of the chamber by means of sulphuric acid, of specific gravity 1.76. On treating the product, technically called "nitrous sulphuric acid," with steam, the nitrous fumes are expelled, and may be again sent into the chamber, the diluted sulphuric acid being of course again concentrated.

All the essential parts of a sulphuric acid chamber are represented in the Frontispiece—*a a* are the burners, *b* contains the

Chili saltpetre to be placed in the flue of the burner, *c* is the pipe through which the gases pass into the chambers, *d* is the steam boiler, *e* is the exit pipe, *f* is the denitrating tower, and *g* the arrangement in which the denitration of the oil of vitriol is effected. The supply of steam into the chamber is so regulated that the specific gravity of the acid is about 1.60. It is found that if the strength be allowed much to exceed this point the liquid absorbs considerable quantities of sulphur dioxide and oxides of nitrogen, and, moreover, attacks the material of the chamber. As soon, therefore, as the "chamber acid" attains the above density it is run off into leaden pans, and concentrated by heating, either from above or from below, until its specific gravity is raised to 1.70.* Other methods of concentration are occasionally made use of. Sometimes the heated sulphur dioxide from the burners is made to pass over the surface of the acid, whereby the nitrous fumes which it contains are again sent into the chamber, together with the aqueous vapour.

The further concentration of the acid is effected in large platinum or glass retorts. Fig. 106 represents a platinum retort. The acid is syphoned over from the pan *a* through the bent funnel tube *b* fitting into the hood of the retort. The syphon *c* is maintained constantly full of liquid; on lowering the vessel *d* to the level of the spout the acid runs over into the tube. The hot concentrated acid is drawn off by a syphon *e*, surrounded with cold water, whereby it is cooled, and is transferred directly to carboys. The glass retorts employed in the concentration are represented in fig. 105. They are simply glass vessels placed in metal pots containing a little sand, and fitted with a movable neck, from which leads a pipe where the acid water is condensed. The acid as run into the retorts has invariably a dark brown colour, from the presence of carbonaceous matter. After several hours' boiling it becomes colourless, from the action of the strong

* It appears that the composition of the lead employed in the manufacture of the pans exerts a remarkable influence upon their durability. Pure soft lead seems to be more rapidly acted upon than the harder metal. By the addition of a small quantity of antimony the pans appear to withstand the action of the acid for a longer period. Compare Hasenclever, *Ber. Deut. Chem. Gesell.*, 1872.

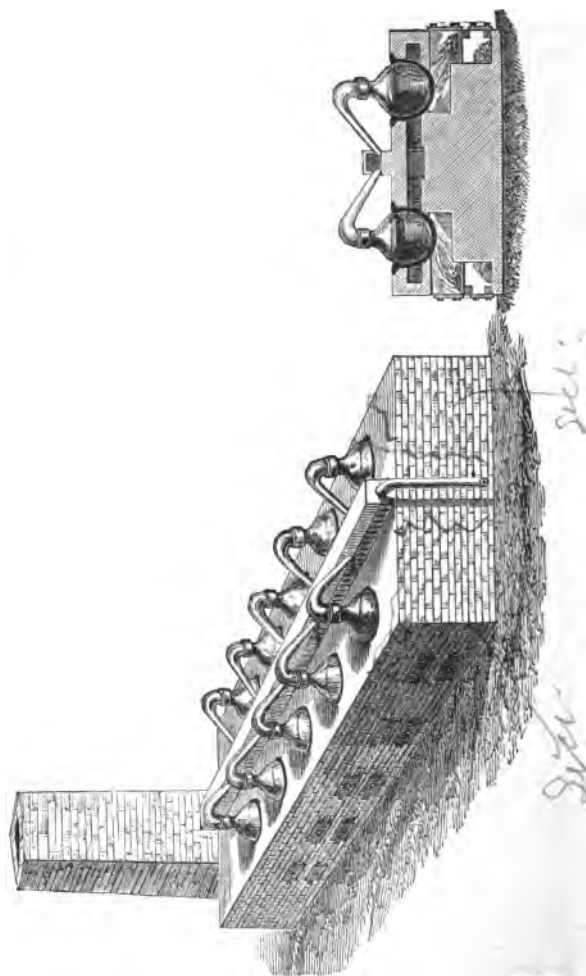


Fig. 105.

acid upon the carbon, which is thereby converted into carbon dioxide at the expense of a small portion of the sulphuric acid which is reduced to sulphur dioxide.

Pure sulphuric acid is a colourless, oily, odourless liquid of sp. gr. 1.854 at 0°. It boils at 338°, and freezes at 10.5°. The strong acid is exceedingly hygroscopic; when exposed to the air it rapidly increases in weight from the absorption of atmospheric moisture. Hence it is frequently used as a desiccating agent. From its powers of abstracting water it is often employed in chemical actions; thus, oxalic acid, when

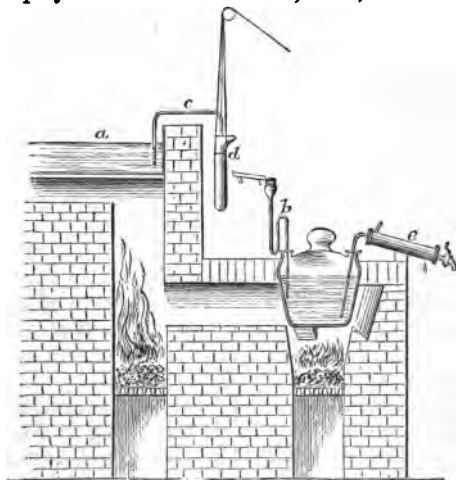


Fig. 106.

heated with the strong acid, is resolved into carbon dioxide and carbon monoxide (p.250), formic acid is converted directly into carbon monoxide (p.250), alcohol into ethene (p.219), &c. Absolutely pure sulphuric acid—*i. e.*, acid of the composition H_2SO_4 —cannot be prepared by simply boiling down a weaker acid under any pressure, at least not under from 3 to 300 centimetres of mercury, an acid of the composition $\text{H}_2\text{SO}_4 \cdot \frac{1}{2} \text{H}_2\text{O}$, or $12\text{SO}_3 \cdot 13\text{H}_2\text{O}$, being invariably obtained by this treatment. The same result is obtained if this hydrate be mixed with sulphur trioxide and redistilled. If this acid ($\text{H}_2\text{SO}_4 \cdot \frac{1}{2} \text{H}_2\text{O}$)

be exposed to a low temperature, pure H_2SO_4 crystallizes out. The crystals melt at $10^\circ\cdot5$, and when gently heated evolve sulphur trioxide, and when boiled form the original hydrate, $\text{H}_2\text{SO}_4\cdot\frac{1}{2}\text{H}_2\text{O}$. It is unnecessary to assume the existence of a stable molecule of the composition $12\text{SO}_3\cdot13\text{H}_2\text{O}$ to account for this phenomenon. When the vapour of sulphuric acid is heated to a moderately high temperature it is dissociated into H_2O and SO_3 , and it is possible that in liquid sulphuric acid some of the molecules may possess the state of motion corresponding to a temperature above that of dissociation. The liberated molecules of H_2O and SO_3 would in all probability unite with the unchanged molecules of H_2SO_4 to form compounds of the formulæ $\text{H}_2\text{SO}_4\cdot x\text{H}_2\text{O}$ and $\text{H}_2\text{SO}_4\cdot x\text{SO}_3$. If we further assume that the latter combination is the less stable, on heating, the trioxide will predominate in the vapour in proportion to the temperature of the liquid—(Dittmar)

A great development of heat is occasioned by mixing the concentrated acid with water; on adding 4 parts by weight of oil of vitriol to 1 part of water the temperature rises from 0° to 100° . On again cooling the mixture to 0° it is found to occupy a less volume than the sum of the volumes of the components. The maximum amount of condensation is about 8 per cent. This amounts to a degree of hydration corresponding to the formula $\text{H}_2\text{SO}_4\cdot2\text{H}_2\text{O}$. A second definite hydrate is known of the composition $\text{H}_2\text{SO}_4\cdot\text{H}_2\text{O}$. It is readily obtained by diluting the strong acid until it has a specific gravity of 1.78. On cooling the liquid to about 7° , it solidifies to a mass of rhombic crystals; hence it is frequently called *glacial sulphuric acid*. It boils at 205° . Both these hydrates produce intense cold when mixed with snow.

The commercial oil of vitriol invariably contains lead sulphate, derived from the action of the acid upon the material of the chamber and concentrating pans; not unfrequently it also contains arsenic (derived from the pyrites), nitrogen oxides, and sulphur dioxide. The latter impurities may be detected by shaking a stoppered bottle half filled with the acid, and testing the air with a slip of iodized starch paper. If the lower oxides of nitrogen are present

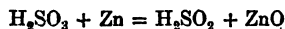
the paper will be quickly turned blue, from the liberation of the iodine and the formation of the blue iodide of starch; if sulphur dioxide be also present, the blue coloration will be gradually destroyed. The acid may be purified from lead sulphate and oxides of nitrogen by simple redistillation after the addition of a small quantity of ammonium sulphate. At about 400° the vapour of the acid is resolved into sulphur trioxide and water, and at a red heat the former compound is further decomposed into sulphur dioxide and oxygen (see p. 325). This decomposition has been proposed as a method of obtaining oxygen. The acid is allowed to drop upon strongly heated bricks, and the resultant gases are passed through water, by which the steam and sulphur dioxide are retained, the oxygen remaining unabsorbed. This, after all, is only a circuitous method of obtaining oxygen from the air, the sulphur dioxide having been originally made and oxidized by atmospheric oxygen.

Sulphuric acid is dibasic: it contains two atoms of replaceable hydrogen. Two series of sulphates are accordingly obtained. Thus, in the case of sodium we have—

Acid Sodium Sulphate or Sodium Hydrogen Sulphate, NaHSO_4 .
 Monosodium Sulphate, Na_2SO_4 .

The greater number of the sulphates are soluble, crystallizable salts, and many of them occur native. The most insoluble of the series are the lead, calcium, strontium, and barium sulphates. The production of the last named salt is used as a test for sulphuric acid. On adding a solution of barium chloride to the acid, or to a solution of a sulphate, a dense white precipitate of barium sulphate is obtained. All sulphates, when heated with charcoal and sodium carbonate in the reducing area of the Bunsen flame (p 238), yield sodium sulphide, the presence of which may be recognized by the black stain of silver sulphide obtained by placing the fused mass upon a silver coin, and moistening it with a drop of water.

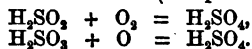
215. Hyposulphurous Acid, H_2SO_2 .—This acid, discovered by Schützenberger, and termed by him hydrosulphurous acid, may be obtained by dissolving zinc in an aqueous solution of sulphurous acid—



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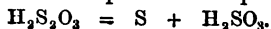
Y

It will be seen that no hydrogen is evolved in the reaction. The solution becomes yellow as the metal dissolves, and possesses greater bleaching powers than sulphurous acid, as the following equations indicate (compare p. 323):—



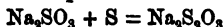
Hyposulphurous acid acts as a powerful reducing agent, precipitating mercury and silver from their solutions. The readiest method of preparing it consists in immersing zinc clippings in a concentrated solution of acid sodium sulphite. The zinc rapidly dissolves with formation of zinc sodium sulphite, $\text{Na}_2\text{Zn}(\text{SO}_3)_2$, which separates out. The supernatant liquid is decanted into a flask, which can be well closed, and is mixed with three or four times its volume of strong alcohol. The greater portion of the zinc sodium sulphite, still left in the solution, rapidly crystallizes out; the clear liquid is again decanted off into a flask, which should be quite filled with it, and then closed by a well fitting cork. In a short time the liquid will solidify to a mass of colourless needles of sodium hyposulphite, NaHSO_3 . This substance is very unstable; it rapidly absorbs oxygen from the air, even when dry, and is thereby converted into sodium hydrogensulphite, NaHSO_3 . Its solution bleaches rapidly, and reduces many metallic salts. To isolate the acid, the salt in aqueous solution is decomposed by oxalic acid. The solution of the acid possesses a deep orange colour, it bleaches strongly, and rapidly decomposes on exposure to air from the absorption of oxygen.

216. Thiosulphuric Acid, $\text{H}_2\text{S}_2\text{O}_3$, or $\left. \begin{smallmatrix} \text{HS} \\ \text{HO} \end{smallmatrix} \right\} \text{SO}_2$. This acid, originally and still commonly called *hyposulphurous acid*, may be regarded as sulphuric acid, in which a moiety of the hydroxyl, HO, has been replaced by the radical sulphhydryl, HS; indeed, it may be obtained by the sulphuration of sulphurous acid, just as the oxidation of that acid produces sulphuric acid. The acid itself cannot be preserved in the free state. On adding hydrochloric acid to a solution of the sodium salt, the liberated thiosulphurous acid is quickly resolved into sulphur and sulphurous acid—



In very dilute solutions, however, the decomposition is not complete even after a long time; after [many weeks' standing, the liquid still gives the reactions of thiosulphuric acid.

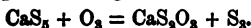
The thiosulphates may be obtained by digesting sulphur with solutions of the sulphites—



—or by boiling sulphur with a solution of an alkaline hydrate, an alkaline pentasulphide being simultaneously formed—



On exposing the deeply coloured solution to the air, it gradually becomes colourless, sulphur being deposited, and a further quantity of thiosulphate being formed—



Advantage is taken of this reaction to make sodium thiosulphite (the most important salt of the series) from gas lime refuse and alkali waste. The resultant calcium salt is decomposed by sodium sulphate or carbonate. Sodium thiosulphate is largely used in photography, on account of its power of dissolving certain insoluble silver salts, *e.g.*, silver chloride, which have not been acted upon by light. It is also used to some extent as an *antichlor*—that is, as an agent for removing the last traces of chlorine from bleached fabrics.

Thiosulphuric acid may be distinguished from sulphurous acid by the precipitation of sulphur which accompanies the liberation of sulphur dioxide when a thiosulphate is treated with hydrochloric acid. Moreover, when a thiosulphate is mixed with iodine solution an iodide and a tetrathionate are simultaneously formed—



Very minute quantities of a thiosulphate in solution may be detected by the deep red coloration afforded by the addition of a solution of a ruthenium salt rendered alkaline by ammonia. Treated with zinc and hydrochloric acid, thiosulphates yield free sulphur and sulphuretted hydrogen.

217. Dithionic Acid, $\text{H}_2\text{S}_2\text{O}_6$.—A manganese salt of this acid may be obtained by passing a stream of sulphur dioxide

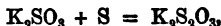
through water containing finely divided manganese dioxide in suspension. The liquid must be kept cold, otherwise but little manganese dithionate will be obtained. The liquid is mixed with barium hydrate, which precipitates manganous hydrate, together with any sulphuric acid which may be simultaneously formed. The filtered solution of barium dithionate is carefully decomposed by an equivalent quantity of sulphuric acid. The solution of the liberated dithionic acid may be concentrated *in vacuo* over oil of vitriol, until it attains a density of 1.347, beyond which it cannot be concentrated without decomposition into sulphuric acid and sulphur dioxide—



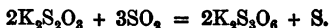
In contact with the air the strongly acid solution is gradually oxidized to sulphuric acid.

The dithionates may be obtained by decomposing the barium salt, obtained as above, by the sulphate of the wished for base. All the salts are soluble in water, and may generally be obtained in well defined crystals, which are permanent in the air. Their solutions, mixed with hydrochloric acid and heated, are decomposed, forming sulphur dioxide and sulphuric acid without precipitation of sulphur.

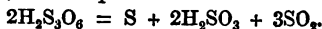
218. Trithionic Acid, $\text{H}_2\text{S}_3\text{O}_6$, is obtained as a potassium salt by warming a solution of acid potassium sulphite with sulphur. The reaction in all probability occurs in two stages; the first phase consisting in the production of potassium thiosulphate—



the thiosulphate thus formed being converted into the trithionate by the action of sulphur dioxide—



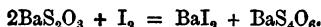
In fact, this salt may be prepared by the direct action of sulphur dioxide upon a solution of an alkaline thiosulphate. The acid itself is permanent in dilute solutions, but on concentration, even *in vacuo*, it is resolved into sulphur, sulphurous acid, and sulphur dioxide—



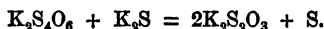
The trithionates are soluble, unstable salts. On heating, their

solutions are decomposed into sulphates, with evolution of sulphur dioxide and precipitation of sulphur.

219. Tetrathionic Acid, $H_2S_4O_6$, may be obtained as a barium salt by the addition of iodine to barium thiosulphate—



Barium thiosulphate is suspended in a small quantity of water, and mixed with iodine in small successive portions. On the completion of the reaction the mass of finely divided crystals is treated with alcohol, which dissolves the barium iodide together with the excess of iodine. The barium tetrathionate remains as a fine white powder, which may be purified by recrystallization from a small quantity of water. The acid may be obtained by decomposing the barium salt by an equivalent quantity of sulphuric acid. It is only stable in dilute aqueous solution unexposed to the air. The potassium tetrathionate is distinguished from the corresponding salt of the other polythionic acids by its reaction with potassium monosulphide, which converts it into potassium thiosulphate with separation of sulphur—



220. Pentathionic Acid, $H_2S_5O_6$, may be obtained by the mutual action of sulphuretted hydrogen and sulphurous acid. A stream of sulphuretted hydrogen is passed into a strong aqueous solution of sulphurous acid, the liquid is filtered and digested with metallic copper until it becomes clear, the dissolved copper is precipitated by sulphuretted hydrogen, and the filtered liquid is concentrated in the water bath until it acquires a density of 1.3. It may be further concentrated by evaporation *in vacuo* until it has a density of 1.6. The solution is permanent at ordinary temperatures, and possesses a strongly acid, bitter taste. On heating, it is resolved into sulphuretted hydrogen, sulphur dioxide, sulphur, and sulphuric acid. Pentathionic acid may also be obtained by treating lead dithionate with sulphuretted hydrogen, or by acting upon sulphur chloride with sulphurous acid.

COMBINATIONS OF CARBON AND SULPHUR.

221. Carbon Bisulphide, Symbol CS_2 .—This compound, also termed *sulphocarbonic acid*, from its analogy to carbon dioxide, was discovered by Lampadius in 1796. It may be obtained by the direct union of its elements. If charcoal is heated to redness in an atmosphere of sulphur, the two substances rapidly combine to form carbon bisulphide. Fig. 107 represents a form of apparatus employed for the production of the bisulphide on the large scale. The charcoal is heated

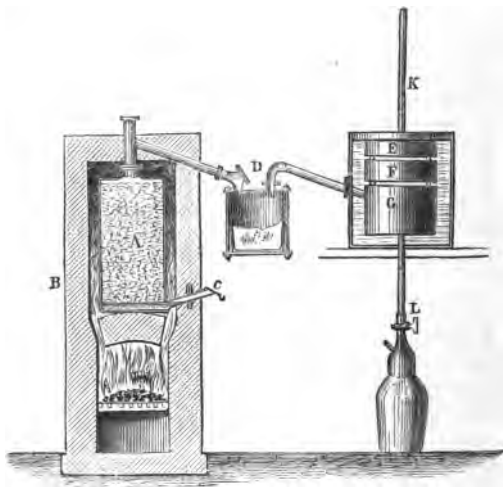


Fig. 107.

in the metal cylinder A, supported in the furnace B. At the bottom of A is a side tube *c*, which can be closed by a lid, through which sulphur is occasionally thrown. The vessel D serves to retain any uncombined sulphur. The cylindrical drums E F G, which are surrounded by water, effect the condensation of the bisulphide which from time to time is drawn off through the cock L. The non-condensable gases make their escape through the pipe K.

Carbon bisulphide is a colourless, mobile, highly refractive

liquid of sp. gr. 1.293 at 0°. It is extremely volatile, and boils at 46°. Its vapour, mixed with air, is highly explosive. A glass rod heated to about 150°, and plunged into the mixture, occasions this explosion. This temperature is insufficient to effect the union of oxygen and hydrogen. Carbon bisulphide is very inflammable, and burns with a blue flame, producing the dioxides of sulphur and carbon. As ordinarily prepared, carbon disulphide possesses a most disgusting smell, due to the presence of small quantities of indeterminate sulphuretted compounds, but when rectified it has a faint ethereal odour, resembling that of chloroform. It is almost insoluble in water, but mixes readily with alcohol and ether.

The applications of carbon bisulphide in the arts mainly depend upon its powers as a solvent. It rapidly dissolves sulphur, iodine, phosphorus, and many gums and resins, such as caoutchouc and gutta percha. It is largely employed in the vulcanization of caoutchouc, and as a substitute for ether in the extraction of quinine and other alkaloids. It is an excellent solvent for oils and fatty matters. The aromatic principles of flowers and seeds, and the active agents in spices, &c., may be extracted unchanged by means of carbon bisulphide.

The vapour of carbon bisulphide exerts a very depressing effect when breathed in quantity. Even when largely diluted with air it occasions headache and nausea. Its poisonous property may be taken advantage of to remove insects from grain, &c. If a few cubic centimetres of the liquid are sprinkled over the grain, the insects are quickly expelled, and their larvæ and ova are killed. On exposing the grain to the air, the last traces of the bisulphide are quickly dissipated. Brazilian houses are not unfrequently infested with a large burrowing ant, termed the *sauba*, which excavates beneath the foundations, and endangers their stability. The vapour of carbon bisulphide has been found to be a most effectual agent in effecting the dislodgment of these insects.

Carbon bisulphide vapour, passed over many metallic oxides heated to redness, forms the corresponding sulphides. These are frequently crystalline, and resemble the naturally occurring minerals. A mixture of carbon bisulphide vapour and sulphuretted hydrogen, when passed over metallic

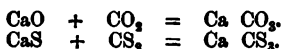
copper heated to redness, yields copper sulphide and marsh gas—



This reaction is interesting, inasmuch as it was made by Berthelot the starting point in a series of syntheses of organic compounds from inorganic sources.

When moist carbon bisulphide is exposed to sunlight a brown, amorphous, odourless powder is obtained, which appears to possess the composition of *carbon sesquisulphide*, C_2S_3 . It is decomposed when heated to about 200° , but is soluble without decomposition in a hot solution of caustic potash. It is insoluble in alcohol, ether, and carbon bisulphide.

Carbon bisulphide acts upon sodium amalgam when the two substances are agitated together. If, on the completion of the reaction, the mass be thrown into water, and the dark red solution be filtered, heated with sulphuretted hydrogen to precipitate the mercury in solution, and then poured into dilute hydrochloric acid, sulphuretted hydrogen is disengaged, and a red flocculent precipitate is obtained, possessing, when purified, the composition $\text{C}_2\text{S}_3\text{H}_2$. This substance may be termed *hydrogen carbosesquisulphide*; or, since it is analogous to glyoxalic acid, $\text{C}_2\text{O}_3\text{H}_2$, it may also be called *thioglyoxalic acid*. The acid melts at about 100° ; it is slightly soluble in ether and alcohol, and readily soluble in carbon bisulphide and alkaline sulphides. When heated with ammonia, and subsequently with chlorine, it yields carbon sesquisulphide (O. Loew). Carbon bisulphide unites with many metallic sulphides to form combinations termed *sulphocarbonates*.

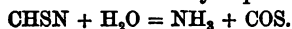


The sulphocarbonates of the alkalis and alkaline earths are soluble, crystalline compounds. When heated with hydrochloric acid, *sulphocarbonic acid*, H_2CS_3 , is obtained as a yellow, oily liquid.

Carbon monosulphide, CS , corresponding to carbon monoxide, has not yet been prepared. The statement of Baudrimont, that it may be obtained by passing the vapour of the

disulphide over red-hot spongy platinum or pumice, has been disproved by Playfair.

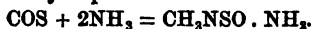
222. Carbon Oxysulphide, COS—Density 30.—This substance, discovered by Than, and believed to exist in certain hepatic waters, may be obtained by the direct union of carbon monoxide and sulphur at a red heat. The gas is absorbed by alcoholic potash, from which it may be liberated by the addition of hydrochloric acid. It is more readily prepared by gently heating potassium sulphocyanate with dilute sulphuric or hydrochloric acids. The liberated sulphocyanic acid is resolved into ammonia and carbon oxysulphide:—



After purification from accompanying hydrocyanic and formic acids, and carbon bisulphide, the oxysulphide possesses an aromatic odour, mixed, however, with that of sulphuretted hydrogen. It burns in the air with a light blue flame, yielding the same products as carbon bisulphide. With oxygen it forms an explosive mixture, and when heated to redness is decomposed into carbon monoxide and sulphur. Carbon oxysulphide is slightly soluble in water, to which it communicates a sweetish taste; after a time its solution is decomposed with formation of carbon dioxide and sulphuretted hydrogen. The same decomposition is immediately effected by dilute alkaline solutions; thus with potassium hydroxide—



Carbon oxysulphide exerts no action upon salts of lead, copper, and silver, in neutral or acid solutions. When moist the gas is decomposed by mercury or finely divided copper and silver with formation of their respective sulphides. It is rapidly decomposed by sodium, even in the cold, and at a red heat with such violence as to occasion an explosion. Carbon oxysulphide unites directly with dry ammonia gas to form ammonium oxysulphocarbamate—

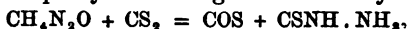


By heating with water in a sealed tube this compound is resolved, by the elimination of the elements of water, into ammonium sulphocyanate—



By treatment with a lead compound the elements of sulphuretted hydrogen are expelled, and *urea* is produced— $\text{CH}_3\text{NSO} \cdot \text{NH}_2 - \text{H}_2\text{S} = \text{CH}_4\text{N}_2\text{O}$.

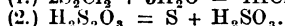
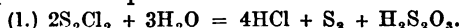
Carbon oxysulphide may indeed be obtained from urea by heating that substance with carbon bisulphide to 110° , ammonium sulphocyanate being simultaneously formed—



COMBINATIONS OF SULPHUR WITH THE HALOGENS.

Chlorine is believed to unite with sulphur in three distinct proportions, although only one of the combinations has been satisfactorily isolated. The two elements slowly unite even at the ordinary temperature; at a gentle heat combination proceeds very rapidly.

223. Sulphur Monochloride, S_2Cl_2 .—Vapour density 67·0. —This, the most stable combination of chlorine and sulphur, is readily obtained by passing a stream of dry chlorine into melted sulphur, or by heating a mixture of sulphur and mercuric or stannic chlorides. When rectified from excess of sulphur or chlorine it forms an amber coloured liquid of a penetrating odour, fuming strongly in the air, and boiling at 136° . Its specific gravity is 1·687. It is gradually decomposed by water into sulphur, hydrochloric and thiosulphuric acids. The last named acid is subsequently resolved into sulphur and sulphurous acid—

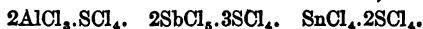


Sulphur monochloride is an excellent solvent for sulphur, a property which leads to its employment in the vulcanization of caoutchouc. At ordinary temperatures a saturated solution contains nearly 70 per cent. of sulphur.

224. Sulphur Dichloride, SCl_2 .—When the monochloride is heated with chlorine it gradually darkens in colour until it becomes brownish red. When subjected to distillation it parts with a quantity of chlorine, and enters into ebullition at about 64° . It appears, however, to be very easily decomposed, and cannot be separated from the accompanying monochloride by fractional distillation. If, however, sulphur

monochloride contained in a freezing mixture is saturated with dry chlorine, the excess of the halogen being afterwards expelled by a current of dry CO_2 , the liquid on analysis is found to contain sulphur and chlorine in the proportion of 1 atom of S to 2 atoms of Cl (Hübner and Guerout). Carius, however, states that this dark red liquid is a mixture of sulphur monochloride and tetrachloride— $\text{S}_2\text{Cl}_2 + \text{SCl}_4 = 3\text{SCl}_2$. Sulphur dichloride appears to be stable when in combination. Thus, with arsenic trichloride it forms a compound possessing the composition— $2\text{AsCl}_3 \cdot \text{SCl}_2$ (Rose); and with ethene and pentene it forms— $\text{C}_2\text{H}_4\text{SCl}_2$, $\text{C}_5\text{H}_{10}\text{SCl}_2$ (Guthrie).

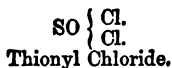
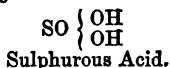
Sulphur tetrachloride, SCl_4 . This compound is only known in combination with certain metallic chlorides, viz.:—



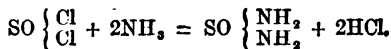
Similar compounds of bromine and iodine with sulphur are believed to exist, but very little is known respecting them.

COMBINATIONS OF SULPHUR WITH THE HALOGENS AND WITH OXYGEN.

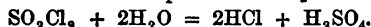
225. Thionyl Chloride, SOCl_2 , may be regarded as sulphurous acid, in which the hydroxyl has been replaced by chlorine—



It stands in exactly the same relation to sulphurous acid that sulphuryl dichloride stands to sulphuric acid (*infra*). It may be obtained by the action of phosphorus pentachloride on sulphur dioxide (Schiff), or by the addition of hypochlorous anhydride to well cooled sulphur monochloride. It is a colourless, strongly refractive liquid of a pungent odour; it has a sp. gr. of 1.675 at 0° , and boils at 78° . It is decomposed by water, forming sulphur dioxide and hydrochloric acid. With ammonia it forms *thionamide*,

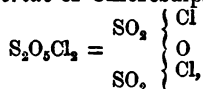


226. Sulphuryl Dichloride, SO_2Cl_2 .—This compound was discovered by Regnault, who obtained it by the direct union of sulphur dioxide and chlorine under the influence of sunlight. When purified it is a colourless, fuming liquid, of specific gravity 1.66, boiling at 77° . It is decomposed by water with formation of sulphuric and hydrochloric acids—

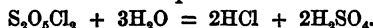


227. Sulphuryl Dibromide, SO_2Br_2 , is a white crystalline substance, which volatilizes unchanged, even at ordinary temperature, and is gradually decomposed by water, producing sulphuric and hydrobromic acids.

Pyrosulphuryl Chloride or Chlorosulphuric Oxide,

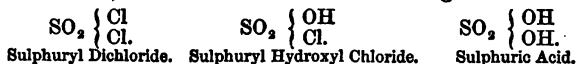


may be obtained by the action of sulphur trioxide upon sulphur monochloride (Rose), or by heating sulphur trioxide with dry sodium chloride (Rosenstiehl), or by the action of phosphorus pentachloride on sulphur trioxide* (Michaelis), or together with phosgene gas by heating carbon tetrachloride with sulphur trioxide (Schützenberger). It is a colourless, oily liquid, of specific gravity 1.819 at 18° ; it boils at 146° . It dissolves slowly and quietly in water, forming hydrochloric and sulphuric acids—



The corresponding bromine compound may be obtained by heating bromoform with sulphur trioxide (Armstrong).

228. Sulphuryl Hydroxyl Chloride, $\text{SO}_2 \left\{ \begin{array}{l} \text{Cl} \\ \text{OH} \end{array} \right.$ —This compound, which was discovered by Williamson, may be regarded as sulphuric acid, in which one atom of chlorine replaces an equivalent quantity of hydroxyl. Its relation to sulphuryl dichloride on the one hand, and to sulphuric acid on the other, will be seen from the following formulæ—

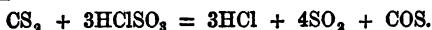


* According to Williamson, these substances give rise to sulphuryl dichloride and phosphoryl trichloride— $\text{SO}_2 + \text{PCl}_5 = \text{SO}_2\text{Cl}_2 + \text{POCl}_3$.

Sulphuryl-hydroxyl chloride may be obtained by distilling a mixture of strong sulphuric acid and phosphoryl chloride—



Or, according to Dewar and Cranston, by passing hydrochloric acid into Nordhausen oil of vitriol. It possesses a specific gravity 1.766 at 18°. It boils at 158°; at about 250° its vapour appears to suffer disassociation into SO_3 and HCl . It is violently decomposed by water, forming sulphuric and hydrochloric acids. When heated with carbon bisulphide it forms hydrochloric acid, sulphur dioxide, and carbon oxy-sulphide—



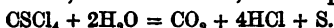
229. A Sulphuryl Nitryl Chloride, $\text{SO}_2 \left\{ \begin{smallmatrix} \text{NO}_2 \\ \text{Cl} \end{smallmatrix} \right.$ is also known.

230. Trichloromethyl Sulphurous Chloride, SO_2CCl_3 , is produced by the action of moist chlorine upon carbon bisulphide. It is a white crystalline substance, insoluble in water, soluble in alcohol and ether. It melts at 135°, and boils at 170°. It has an exceedingly irritating odour; it sublimes, even at ordinary temperatures, in the form of colourless plates. With water it forms hydrochloric and sulphuric acids, sulphur dioxide, and carbon dioxide. Its alcoholic solution, reduced with sulphur dioxide, is supposed to give rise to *dechloromethyl sulphurous chloride*, CHCl_2SO_2 (?).

231. Carbon Sulphochloride, CSCl_2 , the analogue of phosgene gas, COCl_2 is obtained, according to Kolbe, by the prolonged action of *dry* chlorine upon carbon bisulphide. According to Rathke, its formation is facilitated by the presence of iodine. It is a yellow liquid of penetrating odour, which resists the action of water and fuming nitric acid. It is slowly decomposed by caustic potash, forming sulphide and carbonate of potassium, together with carbon tetrachloride.

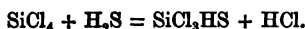
232. Perchlormethyl Mercaptan, $\text{CCl}_3 \left\{ \begin{smallmatrix} \text{Cl} \\ \text{S} \end{smallmatrix} \right.$, discovered by Rathke, is obtained, together with the preceding compound, by the action of chlorine upon carbon bisulphide in presence of iodine. It is a bright yellow liquid of a penetrating odour,

boiling at 146° , and decomposing in presence of water, forming hydrochloric acid, carbon dioxide, and sulphur—



Dilute nitric acid converts it into trichloromethyl sulphurous chloride.

233. Silicon Mercaptan, $\left. \begin{smallmatrix} \text{SiCl}_3 \\ \text{H} \end{smallmatrix} \right\} \text{S}$, analogous to the preceding compound, is obtained by passing a mixture of silicon tetrachloride vapour and sulphuretted hydrogen through a red-hot tube—



It is a colourless liquid, which boils at 196° , and is decomposed by water, forming sulphur, silica, and hydrochloric

acid. With alcohol it yields normal silicon ether, $\text{Si} \left\{ \begin{smallmatrix} \text{OC}_2\text{H}_5 \\ \text{OC}_2\text{H}_5 \\ \text{OC}_2\text{H}_5 \\ \text{OC}_2\text{H}_5 \end{smallmatrix} \right.$

234. Selenium—Symbol Se; atomic weight 79.5.—This substance was discovered by Berzelius in 1817. It is very closely related in its chemical properties to sulphur, and indeed occurs associated with that element in nature. It is found free in monoclinic crystals in certain parts of Mexico, and is a frequent impurity of native sulphur. Selenium is occasionally met with in oil of vitriol obtained from crude sulphur. It also occurs in union with lead, copper, nickel, silver, molybdenum, &c., forming selenides and selenites of these metals. Selenium is principally extracted from a double selenide of lead and copper found in the Hartz, and from certain deposits occurring in vitriol chambers where seleniferous sulphur is consumed.

Selenium occurs in various allotropic modifications, resembling those of sulphur.

235. Amorphous Selenium, obtained by the decomposition of seleniuretted hydrogen, is soluble in carbon bisulphide. The amorphous variety prepared by reducing selenious acid by means of a current of sulphur dioxide, is insoluble in that liquid. On heating, both varieties liquefy at about 100° , and assume the plastic condition. Like the corresponding modification of sulphur, the semi-solid selenium may be drawn out

into long, flexible, transparent threads of a fine ruby-red colour. When quickly cooled after fusion, selenium forms a vitreous mass of a deep brown colour. This modification has a sp. gr. of 4.3, and is nearly insoluble in carbon bisulphide. The vitreous form of selenium remains unaltered at ordinary temperatures, and even after heating to 90°, for some hours; but when the heat is raised to 96°, it rapidly passes into a *crystalline state*. This transformation is accompanied by the development of much heat, and by a change of colour from brown to bluish gray. This modification, which melts at 250°, and is quite insoluble in carbon bisulphide, may also be obtained by exposing an alkaline selenide to the air. Its specific gravity is about 4.8. Selenium is deposited from carbon bisulphide in small monoclinic crystals, resembling those of sulphur. Their sp. gr. is about 4.5. The leaden gray modification of selenium is apparently analogous to rhombic sulphur, the amorphous red variety to the modification of sulphur insoluble in carbon bisulphide. The specific gravities of these two modifications of selenium differ from one another in the same direction as those of the corresponding modifications of sulphur.

At a temperature below a red heat, selenium is converted into a deep yellow vapour, which may be condensed to a finely divided scarlet deposit analogous to that of "flowers of sulphur." Its vapour density, like that of sulphur, is anomalous at temperatures just above its boiling point; at 1420° it becomes normal. The vapour burns with a blue flame, producing an oxide of selenium, possessing a highly characteristic penetrating odour, which has been compared to that of decaying horse radish. Selenium is insoluble in water, but dissolves to a slight extent in strong oil of vitriol. In excess of oxygen gas it burns to selenium dioxide, and on boiling with nitric acid or *aqua regia*, it is converted into selenious acid.

236. Hydrogen Selenide, H_2Se , may be obtained by passing hydrogen and selenium vapour through a red-hot tube, or by acting upon ferrous selenide by sulphuric acid. It is a colourless, inflammable gas, possessing a most intolerable odour. A small quantity of the gas causes violent inflammation of the eyes, and is said to impair the sense of smell for

hours. It is soluble in water. Its solution has an acid reaction, and precipitates many metals as selenides. No selenide of hydrogen corresponding to hydrogen persulphide has yet been obtained.

237. COMBINATIONS OF SELENIUM WITH OXYGEN.—Three selenium oxides are believed to exist, but only one of them, viz., selenium dioxide, SeO_2 , has been isolated. The characteristic odour emitted by selenium when heated is supposed to be due to the formation of an oxide, the composition of which is unknown.

238. Selenium Dioxide, SeO_2 , corresponding to sulphur dioxide, is obtained by burning selenium in oxygen, or by heating selenious acid (*infra*). It is a white, solid substance, which may be obtained crystallized in prisms. It is very hygroscopic. On heating it volatilizes without previous fusion. It is easily soluble in water, forming **Selenious Acid**, $\text{SeO} \begin{cases} \text{OH.} \\ \text{OH.} \end{cases}$. This substance may be obtained in prismatic crystals resembling those of nitre. It is a powerful acid, forming, like sulphurous acid, two classes of salts. Its solution is reduced by sulphur dioxide and sulphuretted hydrogen with deposition of selenium; chlorine and potassium permanganate convert it into selenic acid.

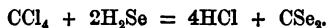
The oxide of selenium corresponding to sulphur trioxide has not been isolated.

239. Selenic Acid, $\text{SeO}_2 \begin{cases} \text{OH.} \\ \text{OH.} \end{cases}$ —The analogue of sulphuric acid, may be obtained as a potassium salt by fusing selenium or the dioxide with nitre, or by the action of chlorine or manganese dioxide upon selenious acid. It is a colourless liquid of specific gravity 2.6, boiling at about 280° . It is very hygroscopic, and when mixed with water occasions a considerable rise of temperature. It dissolves iron and zinc with elimination of hydrogen. The strong acid is reduced to selenious acid on boiling with hydrochloric acid with evolution of chlorine.



Selenic acid is dibasic, and the selenates closely resemble the corresponding sulphates,

240. Carbon Selenide, CSe_2 , appears to be formed by the action of seleniuretted hydrogen upon carbon tetrachloride.



241. Selenium Monochloride, Se_2Cl_2 , is obtained by the direct union of selenium and chlorine, care being taken to maintain the former substance in excess. It is a dark yellow, oily, volatile liquid, decomposed by water, forming hydrochloric and selenious acids together with free selenium. On treating the monochloride with excess of chlorine it is converted into

242. Selenium Tetrachloride, SeCl_4 , a white, crystalline substance which may be sublimed unchanged. It is decomposed by water, forming hydrochloric and selenious acids, $\text{SeCl}_4 + 3\text{H}_2\text{O} = 4\text{HCl} + \text{H}_2\text{SeO}_3$. On exposure to moisture it is converted into

243. Selenium Oxychloride, SeOCl_2 , corresponding to thionyl chloride. This compound may also be obtained by distilling selenium tetrachloride with selenium dioxide. It is a light yellow liquid of specific gravity 2.44, boils at 220° , and is decomposed by water into hydrochloric and selenious acids.

Selenium appears to combine with bromine and fluorine, but nothing is known with certainty respecting these combinations.

Selenium unites with sulphur in two proportions, forming sulphides analogous to the di- and tri-oxides. They are produced by melting the two elements together in the proportions demanded by the formulæ SeS_2 and SeS_3 . They are yellow or red compounds, and may be vaporized unchanged.

244. Tellurium—Symbol Te ; atomic weight 128.—This substance was first recognized as a distinct element by Klaproth in 1798. It is a somewhat rare body, occurring in but few localities. It is found in the free state, and in combination with bismuth, lead, silver, &c. Tellurium is a tin-white metallic looking solid. Its specific gravity is about 6.1. Like all the metals which approximate to the non-metals in chemical characters, it has a great tendency to crystallize. It occurs native in rhombohedral crystals, resembling those of bismuth and antimony. It is very brittle, and may easily

be reduced to powder in a mortar. It melts at about 500° , and at a higher temperature volatilizes as a greenish coloured vapour which condenses in crystalline needles. When heated in the air it takes fire, and burns with a blue flame, forming white fumes of tellurium dioxide. Tellurium is insoluble in water, but, like sulphur and selenium, it dissolves in oil of vitriol, and is precipitated unchanged from its solution by the addition of water.

245. Telluretted Hydrogen, TeH_2 , is a gas possessing a strong resemblance to sulphuretted hydrogen, and obtained by treating a metallic telluride with sulphuric or hydrochloric acid. It burns with a blue flame, has an acid reaction, and dissolves in water, forming a solution which gives characteristic tellurides with many metallic salts.

246. Tellurium Dioxide, TeO_2 , is prepared like the corresponding oxide of selenium. It occurs native as *tellurite* or *tellurium ochre*, a mineral found in Transylvania. Tellurium dioxide is a white crystalline solid which melts to a deep yellow liquid, and may be volatilized. It is but slightly soluble in water.

247. Tellurous Acid, TeO_2H_2 , may be prepared in a similar manner to selenious acid, or by decomposing tellurium tetrachloride with water. It is a white powder possessing a bitter metallic taste. The acid appears to form three classes of salts, viz.—

Neutral Tellurites,	M_2TeO_5
Acid,	MHTeO_5
Hyper Acid,	MHTeO_5
	H_2TeO_5

248. Tellurium Trioxide, TeO_3 , is an orange yellow solid, insoluble in water and in strong acids. It is obtained by heating telluric acid. When strongly heated, it parts with oxygen, and is converted into the dioxide.

249. Telluric Acid, TeO_4H_2 , is easily obtained by fusing tellurium or the dioxide with nitre, dissolving the alkaline tellurate in water, adding barium chloride, washing the insoluble barium tellurate, and decomposing it by dilute sulphuric acid. Telluric acid crystallizes in large hexagonal prisms containing two atoms of water of crystallization; it is freely soluble in hot water. On expelling the water

of crystallization the solubility of the acid decreases considerably.

Telluric acid forms three series of salts corresponding to those formed by tellurous acid. The tellurates are in general insoluble in water, but they dissolve readily in hydrochloric acid.

250. Tellurium Dichloride, TeCl_2 , is formed by heating tellurium in chlorine, or by distilling the tetrachloride (*infra*) with finely powdered tellurium. It is a black, non-crystalline solid, which readily melts to a dark coloured liquid, and forms a purple vapour which, on further heating, becomes yellow.

251. Tellurium Tetrachloride, TeCl_4 , is obtained by treating the preceding compound with excess of chlorine. It is a white crystalline mass which melts to a yellow liquid; it is very deliquescent, and is readily decomposed by water. It forms double salts with many metallic chlorides, analagous to those containing sulphur tetrachloride (see p. 347). The aluminium compound has the composition, $2\text{AlCl}_3 \cdot \text{TeCl}_4$, corresponding to that of the sulphur compound. Tellurium tetrachloride absorbs ammonia gas, forming a light green mass of the composition $4\text{NH}_3 \cdot \text{TeCl}_4$. On heating, it is gradually decomposed with formation of tellurium.

The dibromide and tetrabromide of tellurium are also known; they are red crystalline compounds, obtained by the direct union of their elements. Similar compounds are known of tellurium and iodine. In addition, a hexiodide, TeI_6 , is supposed to exist.

Tellurium combines with sulphur and selenium. Tellurous sulphide, TeS_2 , is formed by the action of sulphuretted hydrogen on a tellurous salt. It is a dark brown powder which dissolves in solutions of the alkaline sulphides, forming a series of salts, termed the *sulphotellurites*. Telluric sulphide, TeS_3 , is obtained by passing a stream of sulphuretted hydrogen into a solution of telluric acid. It is a lustrous black powder, which dissolves in alkaline sulphides to form alkaline *sulphotellurates*.

252. Boron—Symbol B; atomic weight 11.—This element never occurs naturally in the free state. It is found as boric, or boracic acid, BO_3H_3 , in Tuscany, in the Lipari

Islands, &c.; and as tincal or borax in Thibet, Mexico, California, &c.; as boracite or magnesium borate at Stassfurth; as borocalcite and boronatrocalcite in South America. It occurs also in many minerals. Boron was first isolated by Gay Lussac and Thenard, in 1808. They obtained it by heating dehydrated boric acid, or boric anhydride, with potassium. It may also be formed by igniting a mixture of potassium borofluoride with metallic potassium. As thus prepared, it is a dark brown amorphous powder; it is very slightly soluble in water, and when heated to a high temperature *in vacuo*, or in gases which have no action upon it, it experiences a marked increase in density; but even at a white heat it shows no signs of melting or volatilization. When heated to about 300° in air or in oxygen, it burns with a bright light, forming boric oxide, B_2O_3 , the only known oxide of boron. When burned in air, boron nitride is simultaneously produced in small quantity. It is also converted into boric acid by boiling with sulphuric or nitric acid, and when fused with moist alkaline salts, a borate is formed. When ignited with nitre, the oxidation is attended with explosion. Boron combines directly with chlorine and nitrogen, forming the trichloride and the nitride; it also decomposes nitrogen dioxide, forming boric anhydride and nitride.

Boron may be obtained crystallized by heating the amorphous variety with aluminium. It is rapidly dissolved by the molten metal, and on cooling, crystallizes in octahedrons, varying in colour from light yellow to dark red. The crystals have a sp. gr. of 2.63; they are exceedingly hard (whence the name *adamantine boron* given to the variety), and possess a high lustre and refractive power. Adamantine boron is infusible, even in the oxyhydrogen flame, and is only superficially oxidized at the temperature at which the diamond burns. Acids are without action upon it, and it is not oxidized when heated with nitric acid. Potassium sulphate converts it on fusion into boric acid. When heated on platinum foil, it forms a fusible boride of platinum, and perforates the metal.

A graphitoidal modification of boron was formerly thought to exist; but recent experiments have shown that it is a

compound of boron and aluminium of the composition AlB_2 , or Al_2B_4 , which is readily dissolved by nitric acid, and burns in chlorine gas, forming aluminium and boron chlorides. No hydride of boron is known.

253. Boric or Boracic Acid, H_3BO_3 , is easily obtained by gradually adding 1 part of strong sulphuric acid to 3 parts of crystallized borax, dissolved in 12 parts of boiling water. On cooling, the boric acid separates out in shining crystalline scales. All the boric acid of commerce was formerly thus prepared from naturally occurring borax. The acid was first isolated by Homberg, in 1702. He prepared it by heating a mixture of dehydrated ferrous sulphate with borax, the boric acid was carried over with the water, which was simultaneously liberated, and collected in the receiver.

Boric acid is now largely obtained from the lagoons or pools which collect round the *suffioni* or jets of steam which are discharged through earth fissures in the volcanic district of Tuscany. The quantity of boric acid contained in the *suffioni* is exceedingly minute; but by connecting a number of the lagoons together, the water becomes gradually charged to the extent of about 0.5 per cent. The liquid is allowed to clarify by standing, and is concentrated by passing through a series of shallow tanks, heated by several of the jets of steam, which are diverted from their course, and led beneath the bottom of the evaporating pans. The concentrated liquor is run into crystallizing tubs, and the boric acid, which separates out, is dried on the floor of a chamber also heated by naturally formed steam. The product is far from pure; it rarely contains more than three-fourths of its weight of boric acid. Nothing is known with certainty respecting the source of the boric acid in the *suffioni*. A considerable quantity of boric acid is now obtained by decomposing naturally occurring boracite, MgB_2O_4 , and boronatocalcite ($Na_2O \cdot 2B_2O_3$) + $(2CaO \cdot 3B_2O_3)$ + $15H_2O$ (Kraut), which occurs in the province of Tarapaca, in Peru, and in various parts of Chili.

Boric acid crystallizes in nacreous laminae, which are translucent, and have an unctuous feel. The solution has a faint acid reaction, and a bitter taste. The acid exhibits some remarkable irregularities in dissolving in water. It

requires 2.5 parts of water at 18° , and 14.9 parts at 25° . After this point, its rate of solubility increases, and it dissolves in 10.7 parts of water at 50° , in 4.7 parts at 75° , and in 2.97 parts at 100° . This difference in solubility at 25° is, in all probability, due to a change of hydration in the substance. The solubility of the acid is increased by the addition of tartaric acid or a soluble tartrate. Boric acid is soluble in alcohol, and the solution burns with a bright, green-edged flame. Its aqueous or alcoholic solution acidified with hydrochloric acid colours turmeric brown, especially on drying. If the brown spot be moistened with an alkali, it is coloured black.

By heating boric acid to 120° , *metaboric acid*, HBO_2 , is obtained; and at a higher temperature *boric oxide* or *boric anhydride*, B_2O_3 , is produced, which fuses to a viscid liquid below a red heat, and solidifies on cooling to a colourless glass of sp. gr. 1.83. Boric acid requires prolonged fusion to expel the last traces of moisture. Even at 270° it retains about 3 per cent. of water. Boric anhydride is hygroscopic, and on exposure to the air is gradually transformed into the acid by absorption of water. At a white heat it volatilizes unchanged.

The borates are a somewhat complicated class of compounds, from the tendency of the acid to form multiple salts. The most important of the series is borax, $\text{Na}_2\text{H}_3\text{B}_4\text{O}_{10}$, which crystallizes from its aqueous solution in octahedral or in prismatic crystals. These differences depend upon the degree of hydration of the salt. Prismatic or ordinary borax contains 9 atoms of crystalline water. The octahedral variety has only 5 atoms. The formation of the particular variety is dependent upon the temperature of crystallization, and the concentration of the solution.

254. Boron Nitride, BN or B_3N_3 .—Boron displays a marked affinity for nitrogen. It has already been stated that when it burns in the air a portion combines with the nitrogen to form a nitride. Boron nitride may be easily prepared by igniting a mixture of 2 parts ammonium chloride and 1 part dehydrated borax, and washing the resultant mass. It may also be formed by the direct union of its elements, or by heating boron in ammonia gas, or by heating boric oxide with urea. Boron nitride forms a soft, white, inodorous, infusible

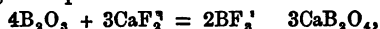
powder, which is insoluble in water and in most acids. Boiling sulphuric acid decomposes it with formation of ammonia, and boric acid; and strong hydrofluoric acid converts it into ammonium borofluoride. When projected into a flame it burns with a greenish light, forming boric oxide. Chlorine is without action upon it, but by fusion with alkalies it is decomposed. No carbide or silicide of boron is known.

255. Boron Chloride, BCl_3 , may be formed by burning boron in chlorine, or by heating a mixture of boric oxide and charcoal in chlorine gas. It is an exceedingly volatile, fuming, highly refractive liquid of sp. gr. 1.35. It boils at 18.2° . It is decomposed by water, forming boric and hydrochloric acids, and is converted into ethyl borate and hydrochloric acid when treated with alcohol. It unites directly with ammonia gas, forming a white crystalline powder which may be sublimed unaltered. Its composition is $3\text{NH}_3, 2\text{BCl}_3$. By passing it through a red hot tube with ammonia gas it is converted into boron nitride.

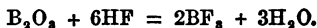
Boron chloride unites with cyanogen chloride with evolution of heat, forming a crystalline mass, BCl_2CyCl , which is decomposed by water and alcohol, with production of hydrochloric and boric acids and gaseous cyanogen chloride.

256. Boron Bromide, BBr_3 , may be formed by the direct union of its elements. It is a colourless, mobile liquid of sp. gr. 2.69, which fumes strongly in the air, boils at 90° , and is decomposed by water and alcohol in a similar manner to the chloride.

257. Boron Fluoride, BF_3 , is a colourless, strongly fuming gas, obtained by heating a mixture of boric oxide and fluor-spar to a high temperature in an iron tube—



Or more readily by heating a mixture of dehydrated borax, fluor-spar, and oil of vitriol in a flask—



As thus obtained, the gas is mixed with a small quantity of silicon fluoride obtained by the action of the hydrofluoric acid upon the flask. Moreover, a portion of the boron fluoride suffers decomposition by the water simultaneously formed. The gas is rapidly absorbed by water, which takes

up about 700 times its bulk, and forms a dense oily liquid having the composition $2\text{BF}_3 \cdot 3\text{H}_2\text{O}$. The gas is also absorbed by oil of vitriol. Ammonia combines directly with boron fluoride to form a white powder, NH_3BF_3 . By prolonged treatment with ammonia this substance is converted into two liquid compounds, $2\text{NH}_3 \cdot \text{BF}_3$ and $3\text{NH}_3 \cdot \text{BF}_3$.

258. Fluoboric Acid, $\text{HBO}_2 \cdot 3\text{HF}$, is obtained by passing boron fluoride into ice-cold water, or by adding boric oxide to hydrofluoric acid contained in a platinum crucible and strongly cooled. It is an oily liquid which fumes in the air and distils unchanged. By the addition of bases a series of salts termed *fluoborates* may be obtained. By treatment with water the acid is decomposed with formation of boric acid and hydrofluoboric acid.

259. Hydrofluoboric Acid, HBF_4 or BF_3HF , is known only in dilute solutions, as it is converted into hydrofluoric and fluoboric acids on concentration. The *borofluorides* are, however, a stable series of salts. They are generally soluble in water, and may be obtained definitely crystallized. The potassium salt, KBF_4 , is, however, only sparingly soluble in cold water.

260. Boron Sulphide, B_2S_3 —the analogue of boron oxide—may be formed by heating boron in sulphur vapour, or boric oxide and charcoal in vapour of carbon bisulphide. It is a white solid substance of a pungent, irritating odour; it volatilizes unchanged in a stream of sulphuretted hydrogen, and is decomposed by water with formation of boric acid and sulphuretted hydrogen. This decomposition is supposed by some to occur in the lagoons of Tuscany, where the boric acid is accompanied by sulphuretted hydrogen. The boric acid is assumed to have originally existed as boron sulphide; on meeting with aqueous vapour this compound is decomposed in accordance with the equation— $\text{B}_2\text{S}_3 + 6\text{H}_2\text{O} = 2\text{H}_3\text{BO}_3 + 3\text{H}_2\text{S}$.

CHAPTER XIII.

THE PHOSPHORUS OR NITROGEN GROUP.

NITROGEN, phosphorus, arsenic, and antimony constitute a family of elements possessed of relationships as intimate as those manifested among themselves by the halogens, or by the members of the sulphur group. The first member of this group, nitrogen, we have already studied; the fourth member, antimony, is generally classed among the metals. In its chemical characters, antimony is closely allied to arsenic on the one hand, and to bismuth on the other; it constitutes, indeed, a connecting link between the metals and the non-metals. The atomic weights of the members of the nitrogen group show the same gradational order which exists in the oxygen and fluorine groups—

N. 14	P. 31	As. 75	Sb. 122
		Mean 76.	
O. 16	S. 32	Se. 79·5	Te. 128
		Mean 79·2	
F. 19	Cl. 35·5	Br. 80.	I. 127
		Mean 80·5	

Roscoe has recently shown that vanadium forms a series of compounds which are strictly analogous to the corresponding phosphorus compounds (see Vol. II.)

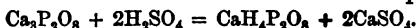
261. Phosphorus—Symbol P; atomic weight 31; density 62.—This substance is one of the most widely diffused of the elements. It is never found uncombined in nature. It exists almost invariably as a metallic phosphate, and mainly as calcium phosphate. Small quantities of this substance are found in the oldest rocks; by their disintegration into soils, the phosphate eventually passes into the plants, and thence into the bodies of animals. Oxidized phosphorus appears, indeed, to be essential to the proper development of animal and vegetable life. In the animal, it is found in the urine, in the blood, in all the soft tissues, and in the bones. The rigidity of bone is in fact due to the presence

of calcium phosphate, which exists therein to the extent of about 58 per cent.

The presence of calcium phosphate in bone may readily be demonstrated by immersing it in moderately dilute hydrochloric acid; in a few hours the greater portion of the earthy matter will have been dissolved away, and the bone will have lost its rigidity; if ammonia be added in excess to the clear solution, the calcium phosphate will be precipitated. The quantity of phosphorus, as phosphoric acid, contained in human urine is very variable. On the average, about 3.2 grams of phosphoric acid are eliminated in the urine during 24 hours (Parkes).

Phosphorus was discovered in 1669 by Brandt of Hamburg, among the products formed by the distillation of the residue obtained by the evaporation of urine. A century later Gahn showed that it was a constituent of bones, and shortly afterwards Scheele devised the process by which phosphorus is now extracted from bone-ash.

Bones are burnt to a white ash, which is finely powdered and mixed with dilute sulphuric acid in sufficient quantity to abstract two-thirds of the lime from the tricalcium phosphate—



The liquid is allowed to deposit the sparingly soluble calcium sulphate, and the clear solution is evaporated to a syrup, when finely powdered wood charcoal is added, and the dried mixture is gradually heated to expel water—



On heating the porous mixture of charcoal and calcium metaphosphate to bright redness, a portion of the phosphorus is eliminated, together with carbon monoxide, and tricalcium phosphate is reproduced—



By mixing sand with the charcoal paste the whole of the phosphorus may be expelled, the calcium phosphate being converted into silicate (Wöhler)—

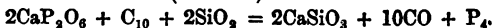


Fig. 108 represents the arrangement in which the distillation is effected. A number of earthenware retorts, *a a*, containing the mixture of charcoal and metaphosphate, and placed

in a furnace, are connected with "adapters," *b b*, which fit into metal or earthenware receivers, *c c*, containing water. The

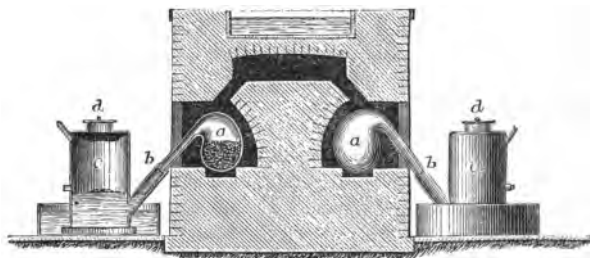


Fig. 108.

receivers are furnished with lids, *d d*, and have each a small tubulus to allow of the escape of the carbon monoxide, &c.

The crude phosphorus contains small quantities of oxides, and of amorphous phosphorus, which give it a brown colour. In this state it is excessively inflammable, and requires to be handled with great care. Formerly its purification was effected by melting it and squeezing it through chamois leather, which retained the solid impurities; or by filtering it through a layer of charcoal. On agitating it with a warm solution of chromic acid, or with a mixture of acid potassium chromate and sulphuric acid, the impurities rise to the surface, and may be skimmed off, and the melted phosphorus gradually becomes colourless and transparent. Phosphorus, as found in commerce, is usually cast into sticks; the moulding was formerly effected by the highly dangerous plan of drawing the melted phosphorus into glass tubes by suction with the mouth. Fig.

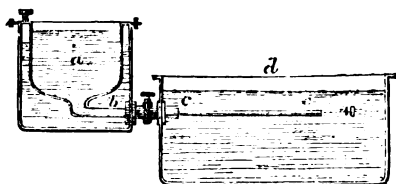


Fig. 109.

109 illustrates an improved method of casting the phosphorus into sticks. The phosphorus is melted in the conical vessel *a*, by warm water, and is allowed to run through the pipe *b*, which can be closed with a stop-cock, into the glass tube *c c*, which is

surrounded by cold water in the trough *d*. A copper wire is placed in the tube *c c*, round which the phosphorus solidifies, and it is easy, by regulating the flow of the phosphorus by means of the stop-cock, to obtain a continuous rod of the solidified substance, which may afterwards be cut into pieces of any desired length. For the use of the match-maker, phosphorus is often cast into cheese-shaped masses. Phosphorus is occasionally granulated by agitating it, when melted, with a warm solution of salt or sugar until it solidifies.

Pure phosphorus is almost colourless, and perfectly transparent when freshly prepared. It melts at 44° to a viscid, oily liquid, which may be cooled even to 32° —*i. e.*, 12° below its melting point, without solidifying, but when touched with a piece of solid phosphorus, or with a glass rod which has been in contact with phosphorus, it instantly solidifies, and its temperature rises to 44° . Its specific gravity is about 1.8. When strongly cooled, phosphorus becomes hard and brittle, and can be cut only with difficulty, but at 25° or 30° it is soft and flexible, and may be bent without breaking. A broken stick of phosphorus exhibits a distinctly crystalline fracture, but large individual crystals can only be obtained by the gradual evaporation of its solution in carbon bisulphide. The normal form of crystallized phosphorus appears to be that of a regular octahedron (?). Phosphorus boils at about 290° . Its vapour density is abnormal; at 1040° it is 62—*i. e.*, the atom of phosphorus occupies only half the bulk of the hydrogen atom. Phosphorus volatilizes even at temperatures below its melting point. If a quantity of phosphorus be sealed up in a flask containing nitrogen, and the lower portion of the flask be immersed in a bath having a temperature of about 40° , the phosphorus sublimes into the upper portion of the flask in colourless microscopic cubic (rhombic ?) crystals of a brilliant lustre. Phosphorus is insoluble in water, but it dissolves readily in sulphur chloride and carbon bisulphide. It is also soluble in benzene and oil of turpentine. Phosphorus is highly inflammable, and burns in the air with a bright white flame, giving off dense fumes of the pentoxide. On account of its great inflammability it is necessary to keep it in water. On pouring a few drops of a solution of phosphorus in carbon bisulphide upon a piece of

paper, and allowing the liquid to evaporate, the finely divided phosphorus left on the paper absorbs oxygen with such rapidity that it bursts into flame. A stick of phosphorus exposed to the air undergoes a slow combustion, and in the dark is seen to be surrounded by a greenish white light (whence the name phosphorus from $\phi\acute{o}\varsigma$, light; and $\phi\acute{\epsilon}\rho\omega$, to bring), the phosphorus being gradually oxidized. If kept in a confined volume of air over mercury the diminution in bulk accurately represents the amount of oxygen contained in the air. The steam from boiling water containing phosphorus is highly luminous in the dark. The luminosity of phosphorus is affected in a remarkable manner by very slight causes. In perfectly pure oxygen, at the ordinary temperature and pressure, phosphorus is non-luminous, but on rarefying the oxygen, or on mixing it with carbon dioxide, hydrogen, or nitrogen, the phosphorus becomes luminous. Very minute quantities of many essential oils, of oil of turpentine, and of olefant gas, destroy the luminosity of the phosphorus in air.

The flame of hydrogen gas, impregnated with phosphorus, produces two characteristic green lines when seen through the spectroscope. This reaction is so delicate that it may be used to detect the presence of phosphorus in iron.

262. Allotropic Modifications.—Phosphorus is capable of existing in various modifications. When immersed in water exposed to light it gradually loses its transparency, and becomes superficially covered with a thin film. This opaque substance was formerly regarded as an allotrope of phosphorus, but the recent experiments of Baudrimont appear to show that it is merely a suboxide of phosphorus. Its formation is apparently due to the presence of oxygen, since it is not produced in de-aerated water. Phosphorus is said to be capable of assuming the *viscous* condition by heating it to near its melting point and suddenly cooling it. If ordinary phosphorus be heated with a minute quantity of iodine, or if it be maintained for some hours at a temperature of about 230° in an atmosphere incapable of acting chemically upon it, it gradually changes in colour, and becomes converted into a dark red mass.

Fig. 110 represents the apparatus in which the conversion of yellow into red phosphorus may be conveniently made

from the small scale. The flask A, immersed in the oil-bath, contains a few grains of yellow phosphorus; the air within the flask is displaced by a current of dry carbon dioxide from B; the long tube c dips beneath the surface of mercury contained in the test-glass



FIG. 102.

d. As soon as the air is replaced by carbon dioxide, the tube c is clamped, and the flask A is gradually heated in the oil-bath to about 230° , and maintained at this temperature for about 24 hours, when the greater portion of the substance will be found to have been transformed into the red modification. This substance is now manufactured on the large scale for the use of the match manufacturer. This form of phosphorus is wholly distinct in its physical characters from ordinary or yellow phosphorus. It is insoluble in carbon bisulphide, turpentine, and phosphorus trichloride, and is

more dense than the ordinary variety, its specific gravity being 2.02. It is more resistant to change when exposed to air and heat, and may be heated to 550° without inflaming. At a few degrees above this point it becomes luminous in the air, and is transformed into the yellow variety, which immediately inflames and is converted into phosphorus pentoxide. Unlike the yellow variety it is non-poisonous and may be handled with impunity. It is not necessary to preserve it under water. In the preparation of the matter above described, red phosphorus is a part of the least trace of crystalline form; it is known after heating amorphous phosphorus. By reheating this substance above 550° it sublimes, and may be condensed upon the cooler portion of the tube in microscopic needles. The purest form of red phosphorus may be obtained in this way by filling a glass tube one-fourth with phosphorus, and the remaining three-fourths with lead, displacing the air by carbon dioxide, sealing the tube and heating it

for several hours in an iron tube containing magnesia. On treating the contents of the tube with dilute nitric acid, the lead alone is dissolved, and the phosphorus is obtained in rhombohedrons, isomorphous with arsenic, antimony, and bismuth, nearly black in colour, and of specific gravity 2.34 at 15°.

263. Properties of Phosphorus.—Phosphorus unites readily with oxygen, sulphur, and the halogens. The greater number of the metals burn in the vapour of phosphorus, and are converted into phosphides. Finely divided phosphorus decomposes water, forming hydrogen phosphide, and reduces sulphurous and sulphuric acids. When boiled with an alkali or alkaline earth, it forms phosphoretted hydrogen and a hypophosphite. It detonates when rubbed with nitre and potassium chlorate; and, when heated to redness with sodium carbonate, it liberates carbon.

264. Manufacture of Lucifer Matches.—Phosphorus enters into the composition of the paste with which lucifer matches are tipped. A lucifer match is merely a splint of wood tipped with sulphur, wax, or paraffin, and dipped into a composition of phosphorus, nitre or potassium chlorate, red lead or manganese dioxide, made into a thick paste with gum or glue. The proportion of phosphorus varies considerably, and is often unnecessarily large; its quantity ranges from 4 or 5 to 30 or 40 per cent. Occasionally a small quantity of colouring matter, as vermilion or Prussian blue, is added, together with a little fine sand to increase the friction. The paste is spread out on a cast-iron table, which is kept at a constant temperature by a water-bath placed underneath, and the splints, arranged in a frame or clamp, are dipped into the composition. After dipping, the matches, still in the frames, are allowed to dry; they are then exposed to a temperature of about 30°, after which they are sorted and packed into boxes.

On account of its excessive inflammability, many attempts have been made to reduce the amount of phosphorus needed for the paste. By dissolving the phosphorus in carbon bisulphide before incorporating it with the rest of the composition it is possible to reduce its proportion to $\frac{1}{3}$ of that now generally used. The fumes of phosphorus are very deleterious to the "dippers," who are liable to a disease of the jaw,

which often ends in necrosis of the bone. The inconveniences attending the use of yellow phosphorus may be partly obviated by the substitution of red phosphorus, which is not readily inflammable, and emits no acid fumes; but from the increased cost of the red phosphorus, and from the larger proportion required by reason of its inertness, its use has found but little favour in this country.

Matches which ignite only when rubbed against a prepared surface are now extensively made. The paste applied to the match head, which has been dipped in the usual manner in sulphur, stearine, &c., has the following composition:—

Potassium Chlorate.....	6 parts.
Antimony Sulphide.....	2 to 3 „
Glue.....	1 „

The phosphorus is contained in the composition on the surface against which the matches are rubbed. It is made up of

Amorphous Phosphorus.....	10 parts.
Oxide of Manganese or Antimony Sulphide.....	8 „
Glue.....	3 to 6 „

It is quite possible to make lucifer matches without the use of phosphorus. Indeed, the earliest matches were tipped with a composition which consisted substantially of antimony sulphide and potassium chlorate. Such matches, however, have not come into general use, probably because their action is not quite so certain as that of the ordinary lucifer. There is no doubt that, if the use of phosphorus could be dispensed with in the manufacture of matches, a great boon would be conferred on the agriculturist. The large quantity of phosphoric acid needed in the manufacture of phosphorus for the use of the match manufacturer would thus find its way directly to the soil.

COMBINATIONS OF PHOSPHORUS AND HYDROGEN.

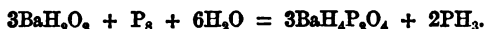
Phosphorus appears to combine with hydrogen in three proportions to form phosphides possessing the composition PH_3 , PH_2 , and P_2H (?).

265. Tri-Hydrogen Phosphide, or Phosphoretted Hydrogen,

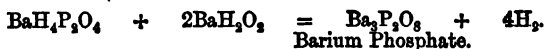
PH_3 .—Molecular weight 34; density 17.—This compound, the analogue of ammonia, cannot conveniently be prepared by the direct addition of hydrogen to phosphorus, hydrogen being without action on melted phosphorus. Hydrogen, however, in the moment of its liberation, appears to unite with phosphorus, since, when the latter substance is placed in contact with zinc and dilute sulphuric acid, phosphoretted hydrogen is produced in small quantity. This gas is evolved in the decomposition of many phosphorized organic bodies; the odour of decaying fish, for example, is due to the formation of phosphoretted hydrogen.

One of the simplest methods of preparing phosphoretted hydrogen consists in decomposing calcium phosphide by the action of water. The calcium phosphide rapidly evolves bubbles of gas, which take fire at the surface of the liquid, and burn with a bright flame, producing white fumes of phosphorus pentoxide. The property of thus spontaneously inflaming is not possessed by pure tri-hydrogen phosphide. The gas evolved from calcium phosphide contains a small quantity of the di-hydrogen phosphide, which may be separated as a liquid by exposing the phosphoretted hydrogen to a low temperature. The di-hydride is exceedingly inflammable, and confers the property of spontaneously inflaming upon any combustible gas with which it may be mixed.

The readiest method of obtaining spontaneously inflammable phosphoretted hydrogen consists in heating phosphorus with an aqueous solution of an alkali, or alkaline earth. In the case of baryta the reaction may be thus represented—



Baryta and phosphorus produce barium hypophosphite and phosphoretted hydrogen. The phosphoretted hydrogen, however, is always mixed with more or less free hydrogen in addition to di-hydrogen phosphide. The hydrogen is produced by a secondary action of the baryta upon the barium hypophosphite; thus—



The quantity of the hydrogen increases with the concentra-
 10.—VOL. I. 2 A

tion of the solution, and towards the end of the reaction it is evolved in comparatively large amount. This secondary reaction occurs to a greater extent when caustic potash is used; accordingly, the alkaline earths are best adapted for the preparation of phosphoretted hydrogen. Fig. 111 represents the apparatus employed in the preparation of this gas. The

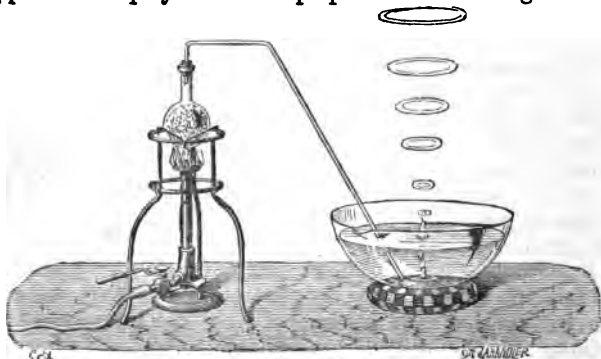


Fig. 111.

small flask contains the phosphorus and baryta water; it is advisable to displace the air above the liquid in the flask by a current of carbon dioxide or coal gas before applying heat, otherwise there is a risk of explosion. Each bubble of gas as it rises to the surface of the water in the trough inflames, burns with a highly luminous flame, and generates a ring-shaped cloud of phosphorus pentoxide, which gradually widens as its ascends.

Non-spontaneously inflammable phosphoretted hydrogen is produced by the action of an alcoholic solution of potash upon phosphorus; less hydrogen is in this case evolved than with aqueous potash. It appears, from the recent experiments of Hofmann, that the perfectly pure gas can only be obtained by the action of caustic potash upon phosphonium iodide (*infra*), a substance which stands to trihydrogen phosphide in the same relation that ammonium iodide stands to ammonia. The decomposition of the phosphonium iodide is analogous to that which ensues when ammonium iodide is heated with caustic potash—



It is remarkable that the property of spontaneously inflaming can be given to the pure gas by allowing it to bubble through strong nitric acid containing a trace of nitrous acid. On the other hand, this property can be destroyed by passing the gas over charcoal, or by exposing it to sunlight, or by mixing it with the vapour of alcohol, turpentine, &c.

Phosphoretted hydrogen is a colourless, inflammable gas, which may be condensed to a liquid by cold and pressure. It has the odour of stinking fish; it is slightly soluble in water, to which it communicates its characteristic smell. It is readily decomposed when subjected to the action of induction sparks. In the apparatus represented on p. 192, 2 vols. of phosphoretted hydrogen liberate 3 vols. of hydrogen, the phosphorus being deposited as a brown powder on the sides of the tube. It is advisable to substitute carbon points for the wires in the eudiometer, since the liberated phosphorus is apt to combine with the strongly heated platinum to form a fusible compound which interferes with the regularity of the discharge.

Phosphoretted hydrogen, from its analogy to ammonia, is sometimes termed *phosphamine*; it possesses, however, no alkaline reaction. It forms addition products with hydrobromic and hydriodic acids, analogous to those produced by ammonia.

266. Phosphonium Iodide or Hydriodate of Phosphamine, PH_3HI , may be obtained by the action of water upon a mixture of iodine and amorphous phosphorus. Böyer gives the following method, as yielding the best results:—100 grams of ordinary phosphorus are dissolved in dry carbon bisulphide, contained in a retort, and the solution is cooled and mixed with 175 grams of iodine, in small portions at a time. The carbon bisulphide is distilled off, the last portions of the liquid being expelled by a current of dry carbon dioxide, and a long and wide tube, not too thick in the glass, is adapted to the neck of the retort. Through the tubulus of the retort is fitted a funnel provided with a stop-cock, by means of which about 50 grams of water can little by little be poured over the phosphorus iodide in the retort. This substance

is immediately decomposed with formation of phosphonium iodide, which, after the addition of the whole of the water, may be sublimed into the wide glass tube, where it condenses in thick white crusts resembling sal-ammoniac. Phosphonium iodide is readily obtained in well defined cubes which deliquesce in the air, and, with excess of water, yield phosphamine and hydriodic acid.

Liquid phosphoretted hydrogen (Dihydrogen Phosphide, PH_3 ?) was discovered by P. Thenard, who assigned to it the foregoing formula. It is the substance which confers spontaneous inflammability upon phosphoretted hydrogen, prepared by the action of baryta or potash upon phosphorus, or by the action of water upon calcium phosphide. 1 part of this substance will communicate this property to 500 parts of any combustible gas. It is a colourless inflammable liquid, which does not solidify at 20° , and is decomposed by a slight elevation of temperature. Prolonged exposure to light resolves it into ordinary phosphoretted hydrogen, and a *yellow solid substance*, which is supposed to have the composition P_2H or P_4H_2 . When spontaneously inflammable phosphoretted hydrogen, standing over water in the pneumatic trough, is exposed to sunlight, it deposits this yellow substance upon the sides of the vessel in which it is confined, and loses the property of inflaming in contact with air. The same substance is also readily formed by transmitting the spontaneously inflammable gas through strong hydrochloric acid, hence the acid destroys the spontaneous inflammability of phosphoretted hydrogen.

OXIDES AND OXIACIDS OF PHOSPHORUS.

Two well defined oxides of phosphorus are known, viz.—phosphorus trioxide, P_2O_3 , and phosphorus pentoxide, P_2O_5 ; these compounds unite with water to form acids which are respectively known as phosphorous acid, $\text{P}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ or PH_3O_3 , and phosphoric acid, $\text{P}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$ or PH_3O_4 . A third oxiaacid of phosphorus is known, viz.—*hypophosphorus acid*, PH_3O_2 , the oxide corresponding to which has not been isolated. Phosphine protoxide, PH_3O , corresponding to hydroxylamine,

NH_3O , is also unknown, although the analogously constituted chlorine and ethyl compounds, PCl_3O and $\text{P}(\text{C}_2\text{H}_5)_3\text{O}$, have been prepared.

A *suboxide of phosphorus*, possessing the composition P_4O , is supposed to exist. It is a yellow powder, which becomes bright red on heating. It is permanent in the air, and may be heated to 300° without alteration.

267. Hypophosphorous Acid, PH_3O_2 , may be obtained as a barium salt by warming baryta water with phosphorus, precipitating the excess of baryta with carbonic acid, filtering and evaporating the solution until the salt separates out. On treating the salt in solution, with an equivalent amount of sulphuric acid, and filtering from the barium sulphate, a solution of hypophosphorous acid is obtained, which may be concentrated *in vacuo* until it becomes viscid. It has a strong acid reaction, and on exposure to the air is gradually oxidized to phosphorous and phosphoric acids. On heating, it is decomposed into phosphoretted hydrogen and phosphoric acid, $2\text{PH}_3\text{O}_2 = \text{PH}_3 + \text{PH}_3\text{O}_4$. In contact with zinc and sulphuric acid it is entirely converted into phosphine. When heated to about 60° with copper sulphate, it forms a red precipitate of *copper hydride*, CuH . This reaction is characteristic of this acid.

Hypophosphorous acid is monobasic. Its salts are all soluble in water and are permanent in the air, but in solution they are gradually oxidized. When heated they evolve water and phosphine (which is generally spontaneously inflammable), and leave a pyrophosphate, or a mixture of pyro- and meta-phosphate, together with a little phosphorus.* The hypophosphites in solution act as reducing agents; on boiling with caustic potash they evolve hydrogen—



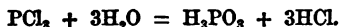
268. Phosphorus Trioxide, P_2O_3 , is said to be formed by the combustion of phosphorus in a limited supply of air or oxygen. It forms white volatile flakes of a garlic-like smell; it is exceedingly deliquescent, and evolves great heat in the act of combining with water. According to Blondlot, the direct action of oxygen on phosphorus produces only the

* Rammelsberg, *Journ. Chem. Soc.*, Jany. 1873.

pentoxide; the white fumes surrounding phosphorus when exposed to air consist entirely of phosphorus pentoxide.

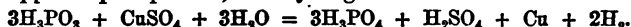
269. Phosphorous Acid, PH_3O_3 , may be obtained by immersing sticks of phosphorus in a saturated solution of copper-sulphate contained in a well closed flask. A black copper phosphide is formed together with a solution of phosphorous and sulphuric acids, the latter of which may be removed by adding baryta water. The solution may be concentrated *in vacuo* until it becomes oily; on strongly cooling the liquid, solid phosphorous acid separates out.

Phosphorous acid may also be obtained by passing a current of chlorine through melted phosphorus covered with a layer of water. Phosphorus trichloride is first produced, which in contact with water forms phosphorous and hydrochloric acids—

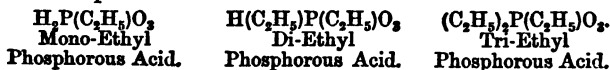


Phosphorous acid may also be conveniently prepared by heating the trichloride with crystallized oxalic acid.

Phosphorous acid separates out from its concentrated solution in crystals which melt at 74° . The acid is exceedingly deliquescent; it is decomposed on heating into phosphine and phosphoric acid, $4\text{PH}_3\text{O}_3 = \text{PH}_3 + 3\text{PH}_3\text{O}_4$, and is gradually oxidized to phosphoric acid in contact with air. It is a powerful reducing substance, especially when in combination with ammonia. When boiled with copper sulphate, metallic copper is precipitated, and hydrogen is evolved—



Phosphorous acid is generally regarded as dibasic, two only of the hydrogen atoms being capable of replacement by metals. Phosphorous ethers are, however, known in which one, two, or three atoms of the hydrogen are replaced by alcohol radicals. But it is worthy of note that only two atoms of the alcohol radicals can be displaced by metals. To denote this fact the composition of the ethyl-phosphorous acids may be thus represented—

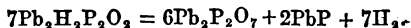


The metallic phosphites are permanent, both in the dry

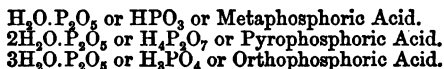
state and in solution, when exposed to air. On heating, some are resolved into pyrophosphates with evolution of hydrogen, *e. g.*—



Others, and particularly those of the heavy metals, are converted, with evolution of hydrogen, into pyrophosphates and phosphides, *e. g.*—



270. Phosphorus Pentoxide, P_2O_5 , is formed when phosphorus burns in excess of air or oxygen. It is a soft, white, amorphous powder, which may be sublimed unchanged. When heated with charcoal it yields phosphorus and carbon monoxide. It is exceedingly deliquescent, and hisses when thrown into water, from the energy with which it unites with that liquid. It combines with water in three proportions, forming—



271. Orthophosphoric Acid, or *ordinary phosphoric acid*, H_3PO_4 , may be obtained by dissolving the pentoxide in water, and boiling the solution. It is also formed when phosphoretted hydrogen burns in the air, $\text{PH}_3 + 2\text{O}_2 = \text{PH}_3\text{O}_4$. It occurs naturally in bone earth, apatite, wavellite, and many other minerals. When these substances are heated with sulphuric acid, they are decomposed with the elimination of phosphoric acid, and the formation of a sulphate.

Phosphoric acid is readily formed by the action of nitric acid upon phosphorus. Small quantities of phosphorus are heated in a retort with moderately dilute nitric acid (sp. gr., 1.2), and the liquid is evaporated until it becomes syrupy. By prolonged heating, the syrupy liquid is partially resolved into pyrophosphoric and metaphosphoric acids; by adding water and boiling the liquid, the acid is reconverted into the ortho modification. On placing its solution, concentrated to a thin syrup, over oil of vitriol *in vacuo*, phosphoric acid is deposited in hard, transparent prisms.

Orthophosphoric acid forms three classes of salts, termed

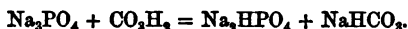
Monometallic orthophosphates, MH_2PO_4 , and $M'H_4P_2O_6$.

Dimetallic orthophosphates, M_2HPO_4 , and $M'H_2PO_4$.

Trimetallic orthophosphates, M_3PO_4 , and $M_3P_2O_6$, and $M''PO_4$.

Where M, M', and M'', denote respectively a mono, di, and tri-atomic metal.

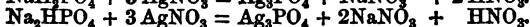
The soluble trimetallic phosphates have a strong *alkaline* reaction, and are readily decomposed by carbonic acid, forming a dimetallic phosphate and an acid carbonate, thus—



The soluble dimetallic salts have a *neutral* or faintly alkaline reaction; the best known members of the series are the sodium salt, $Na_2HPO_4 + 12 H_2O$, and microcosmic salt, $NH_4NaHPO_4 + 4H_2O$.

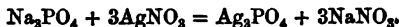
The monometallic salts have a strong *acid* reaction; they are all soluble in water; those of the alkalis and alkaline earths are crystallizable, but those of the heavy metals are permanent only in solution.

All the soluble orthophosphates, whether of the first, second, or third series, give, with silver nitrate, a *light yellow* precipitate of triargentic orthophosphate, Ag_3PO_4 , which is soluble in nitric acid and ammonia. On adding a neutral solution of silver nitrate to a solution of monosodium phosphate and of disodium phosphate, triargentic phosphate, sodium nitrate, and free nitric acid are formed, thus—



Accordingly, the precipitation of the argentic phosphate is incomplete until the free nitric acid is neutralized.

With trisodium phosphate the liquid becomes neutral after the addition of the silver nitrate; hence the whole of the argentic phosphate is precipitated immediately—



The trimetallic orthophosphates, containing fixed bases, are unaltered on ignition; but the mono- and di-metallic phosphates are respectively converted into meta- and pyrophosphates. When ignited with charcoal, the trimetallic

phosphates of the alkalis and alkaline earths are undecomposed, but the mono- and di-metallic phosphates yield phosphorus and trimetallic phosphates.

A solution of ammonium molybdate in nitric acid gives, with a warm solution of an orthophosphate, a bright yellow precipitate of ammonium phosphomolybdate, which is insoluble in acids, but readily soluble in ammonia.

A solution of magnesium sulphate or chloride, mixed with ammonium chloride and ammonia, gives, with solutions of phosphates, a white crystalline precipitate of magnesium ammonium phosphate, $Mg_2(NH_4)_2P_2O_8 + 12H_2O$. This substance is soluble in acids, but highly insoluble in water containing ammonia in solution.

Uranic nitrate and ferric chloride give, with the soluble orthophosphates, yellowish white precipitates, soluble in hydrochloric acid and ammonia, but insoluble in acetic acid.

Mercurous nitrate gives a white precipitate, with the soluble orthophosphates, soluble in nitric acid. Bismuth nitrate also gives a white precipitate of bismuth phosphate, Bi_2PO_4 , which is insoluble in nitric acid. All the foregoing reactions are frequently employed for the recognition and estimation of phosphoric acid.

272. Metaphosphoric Acid, HPO_3 , is formed on dissolving phosphorus pentoxide in cold water, or by strongly heating ordinary phosphoric acid. It forms a colourless, vitreous mass, which dissolves abundantly in water; in solution it is gradually converted into orthophosphoric acid at ordinary temperatures; the transformation is quickly effected on boiling the liquid.

The metaphosphates may be obtained by igniting a mono-metallic orthophosphate of fixed base, or a dimetallic orthophosphate containing one fixed and one volatile base (*e.g.*, microcosmic salt), or by heating trimetallic orthophosphates with phosphoric pentoxide—

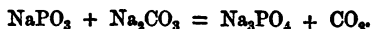


The metaphosphates are non-crystalline fusible salts. They are distinguished from the orthophosphates by giving a *white* precipitate with silver nitrate. Metaphosphoric acid coagulates albumen; orthophosphoric acid is unable to effect this change.

The soluble metaphosphates are converted into orthophosphates on boiling their solutions. Those of the heavy metals, *e. g.*, of silver, are transformed by boiling water into a trimetallic orthophosphate and orthophosphoric acid—

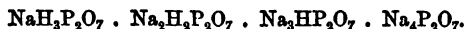


A metaphosphate, on heating with an oxide, hydroxide, or carbonate, is converted into a trimetallic phosphate with elimination of carbon dioxide—



273. Pyrophosphoric Acid, $\text{H}_4\text{P}_2\text{O}_7$, may be obtained by heating syrupy phosphoric acid to 215° . It forms a glassy mass, which cannot be distinguished outwardly from metaphosphoric acid. Its solution does not coagulate albumen; after being neutralized it gives a white precipitate with silver nitrate; on heating to redness it is converted into metaphosphoric acid, and on boiling with water it is transformed into the ortho acid.

Pyrophosphoric acid is tetrabasic, and forms, therefore, four classes of salts; thus, with sodium we have—



Of these the most important is the tetrasodium, or neutral pyrophosphate. It is readily obtained by igniting the disodium orthophosphate. When recrystallized from water it forms monoclinic prisms, which are permanent in the air, and have the composition $\text{Na}_4\text{P}_2\text{O}_7 + 10\text{H}_2\text{O}$. By long continued boiling the pyrophosphates when in solution are converted into orthophosphates. The soluble pyrophosphates may be distinguished from the meta- and ortho-phosphates by the formation of an orange-coloured precipitate with a solution of *luteo*-cobaltic chloride.

By fusing together a mixture of sodium pyrophosphate and metaphosphate in the proportion of 1 atom of the former to 2 of the latter, Fleitmann and Henneberg obtained a salt of the composition $\text{Na}_6\text{P}_4\text{O}_{13} = \text{Na}_3\text{PO}_4 \cdot 3\text{NaPO}_3$, which is soluble in water without decomposition, and may be obtained crystallized by evaporating its solution over oil of vitriol. Other and insoluble phosphates of analogous composition may be obtained from the sodium salt by double decomposition.

By fusing together 1 atom of sodium pyrophosphate with 8 atoms of the metaphosphate, a salt of the composition $\text{Na}_{12}\text{P}_{10}\text{O}_{81} = \text{Na}_3\text{PO}_4 \cdot 9\text{NaPO}_3$ is obtained, which gives by double decomposition salts analogous in constitution.

The mutual relations of these different phosphates may be thus shown—

Orthophosphate,.....	6M ₂ O . 2P ₂ O ₅ ,
Pyrophosphate,.....	6M ₂ O . 3P ₂ O ₅ ,
Fleitmann and Henneberg's salt (1),.....	6M ₂ O . 4P ₂ O ₅ ,
" " "	6M ₂ O . 5P ₂ O ₅ ,
Metaphosphate,.....	6M ₂ O . 6P ₂ O ₅ .

Vanadates of thallium of similar composition have been recently obtained by Roscoe and by Carnelley.*

COMBINATIONS OF PHOSPHORUS WITH THE HALOGENS.

Phosphorus takes fire in an atmosphere of chlorine, and burns with a greenish-yellow flame, producing phosphorus trichloride, PCl_3 , which, as it cools, takes up an additional molecule of chlorine and is transformed into the pentachloride, PCl_5 .

274. Phosphorus Trichloride, PCl_3 , may easily be obtained by passing a slow stream of dry chlorine through melted phosphorus, or through a solution of phosphorus in carbon bisulphide. The two substances rapidly combine, and at a gentle heat the trichloride distils over. If carbon bisulphide has been used, it is separated from the trichloride by fractional distillation. The trichloride may also be obtained by heating phosphorus with mercuric chloride.

Phosphorus trichloride is a colourless mobile liquid of sp. gr. 1.61. It boils at 78°. It absorbs chlorine to form the pentachloride, and oxygen at a boiling heat to form phosphoryl trichloride, POCl_3 .

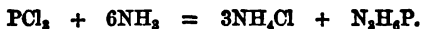
It is gradually decomposed by water, forming hydrochloric and phosphorous acids—



With hot water the reaction is very violent; it is attended

* *Journ. Chem. Soc.*, April, 1873.

with combustion and with the separation of amorphous phosphorus. It rapidly absorbs ammonia, forming a mixture of sal-ammoniac and *phosphoroso-triamide*—



When heated out of contact with air the mixture evolves ammonia and sal-ammoniac, and leaves *phosphoroso-diamide*, $\text{N}_2\text{H}_3\text{P}$, which, on continued heating, is further resolved into *phosphoroso-monamide*, NP.

Phosphorus trichloride, when heated to 80° with phosphorous acid, yields a yellow amorphous powder, which has the composition P_2HO . It is a very stable substance, and may be heated to 250° without change. It resists the action of most solvents at ordinary temperatures, but on heating with water to 170° , it evolves phosphine (Gautier).

275. Phosphorus Pentachloride, PCl_5 , is formed by the action of chlorine upon the trichloride. It is a straw-coloured mass which, by fusion under pressure, may be obtained in prismatic crystals. It is readily soluble in carbon bisulphide, from which it separates in rhombs (Brodie). When heated in the air it sublimes without previous fusion, but under pressure it melts at 148° . When strongly heated its vapour dissociates into PCl_3 and Cl_2 . It rapidly attacks many metals when heated with them, forming phosphorus trichloride and metallic chlorides, which frequently unite with the excess of the pentachloride.

The pentachloride is readily decomposed by water. When exposed to moist air it fumes strongly, and is gradually converted into phosphoryl trichloride and hydrochloric acid—



It contact with excess of water it forms phosphoric and hydrochloric acids—



We have already described its reactions with sulphur dioxide and sulphur trioxide. Phosphorus pentachloride rapidly absorbs ammonia, forming, among other products, *chlorophosphamide*, $\text{N}_2\text{H}_4\text{PCl}_2$. This substance, on treatment with water, yields phosphodiamide, PON_2H_3 , as a white powder, insoluble in water and acids, and but slowly oxidized

on fusion with nitre. On heating out of contact with air it is converted, with elimination of ammonia, into *phosphomamide* or phosphonitrile, PNO.

If the product of the action of ammonia on phosphorus pentachloride be strongly heated in a stream of carbon dioxide, it yields *phospham*, PHN_2 , as a bulky white powder, which may be ignited out of contact with air without alteration. On heating with caustic potash it evolves ammonia, and is converted into potassium pyrophosphate.

If the products of the action of ammonia upon the pentachloride be distilled with water, thin six-sided tabular crystals of *phosphorus chloronitride*, $\text{P}_3\text{N}_3\text{Cl}_6$, are formed in the receiver. These are readily soluble in ether and carbon bisulphide. The chloronitride is slightly volatile at ordinary temperatures, melts at 114° , and boils at 250° . *In vacuo* the substance boils at 160° . It is a remarkably stable substance, and may be heated with sulphuric and hydrochloric acids without alteration. By long continued boiling with fuming nitric acid it is gradually oxidized. Its alcoholic solution boiled with ammonia or potash yields *pyrophosphodiamic acid*, $\text{P}_2(\text{NH}_2)_2\text{H}_2\text{O}_5$.

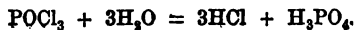
276. Phosphoryl Trichloride, POCl_3 , may be obtained, as already stated, by the limited action of water upon the pentachloride. It may also be formed by the action of dehydrated oxalic acid, or crystallized boric acid upon phosphorus pentachloride—



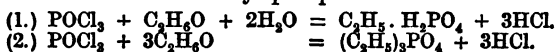
It may also be easily prepared in a state of purity by heating a mixture of the pentoxide and pentachloride under pressure—



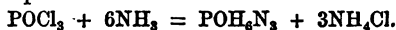
It is a colourless liquid of sp. gr. 1.682 at 19° , boiling at 110° , and solidifying when strongly cooled, especially in contact with a solid body, to a mass of colourless, needle-shaped crystals, which melt at -1.5 (Geuther and Michaelis); at $+2.5$ (Thorpe). It is decomposed by water with formation of hydrochloric and phosphoric acids—



With aqueous alcohol it forms *monoethylphosphoric acid*, and with absolute alcohol triethyl phosphate—

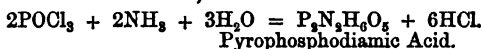


Phosphoryl trichloride, when heated with zinc filings to a temperature above the boiling point of mercury, is slowly reduced to phosphorus trichloride with formation of a vitreous mass, probably consisting of a combination of zinc chloride, and unreduced oxychloride (the $\text{ZnCl}_2 + \text{POCl}_3$ of Casselmann?) mixed with zinc oxide or zinc oxychloride.* Phosphoryl trichloride heated with ammonia forms among other products phosphotriamide—

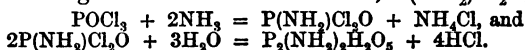


The mass when heated with water leaves phosphotriamide as a white amorphous powder. It is a very stable substance, and may be heated with alkalis and dilute acids without decomposition. It is dissolved by strong sulphuric acid, and is decomposed by *aqua regia*. Fused potash converts it into potassium phosphate with elimination of ammonia.

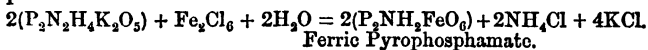
The action of ammonia upon phosphoryl trichloride at a low temperature gives rise to *pyrophosphodiamic acid*, which dissolves as an ammonium salt when the saline mass, after the completion of the reaction, is treated with water—



The reaction in all probability occurs in two stages; the first phase being the formation of an amide, $\text{P}(\text{NH}_2)\text{Cl}_2\text{O}$, thus—



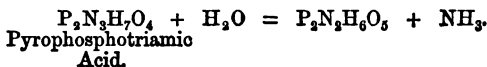
Pyrophosphodiamic acid is dibasic. Its salts may be represented by the general formula, $\text{P}_2\text{N}_2\text{H}_4\text{M}_2\text{O}_5$. When the alkaline salts of this acid are heated with an acidified solution of a copper or ferric salt, a precipitate of cupric or ferric *pyrophosphamate* is obtained, and ammonium chloride passes into solution. Thus with ferric chloride—



* (Thorpe) *Phil. Mag.*, S. 4, 42, 305.

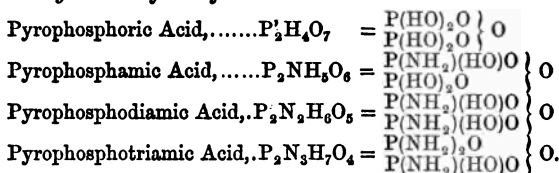
The ferric salt is a white flocculent precipitate. Its production affords a characteristic test for the acid.

The acid itself may be obtained by decomposing the silver salt with hydrochloric acid; it is a semi-fluid, strongly acid, non-crystallizable mass. It is deliquescent, and may be heated to a high temperature without decomposition. It is a tribasic acid. On saturating phosphoryl trichloride with dry ammonia gas, heating the white solid mass to 220° , and boiling with water for a short time, *pyrophosphotriamic acid* is formed, together with pyrophosphodiamic and hydrochloric acids. It is a white, non-crystalline powder, which, when boiled with water for some time, is gradually converted into pyrophosphodiamic acid and ammonia—



Pyrophosphotriamic acid is tetrabasic. All its salts, even those of the alkalis, are nearly insoluble in water.

The phosphamic acids may be regarded as derived from pyrophosphoric acid, by the substitution of 1, 2, and 3 atoms of *amidogen* for hydroxyl. Thus—



A phosphorus oxychloride, of the composition PO_2Cl , corresponding to metaphosphoric acid, and which therefore may be termed *metaphosphoryl chloride*, is formed by heating phosphorus pentoxide and phosphoryl trichloride together for some hours in a sealed tube; it is a viscid, transparent substance (Gustavson). Its formation may be thus formulated— $\text{P}_2\text{O}_5 + \text{POCl}_3 = 3 \text{PO}_2\text{Cl}$.

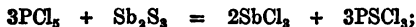
277. Pyrophosphoryl Chloride, $\text{P}_2\text{O}_3\text{Cl}_4$, or $\left. \begin{array}{l} \text{P}(\text{Cl}_2)\text{O} \\ \text{P}(\text{Cl}_2)\text{O} \end{array} \right\} \text{O}$, corresponding to pyrophosphoric acid, may be obtained by the action of nitrogen tetroxide upon well cooled phosphorus

trichloride. It is a colourless, fuming liquid, which boils at about 212° , with slight decomposition. Its sp. gr. is 1.58 at 7° . It decomposes in contact with water, forming orthophosphoric and hydrochloric acids (Geuther and Michaelis).

278. Phosphorus Sulphochloride, PSCl_3 , the sulphur analogue of phosphoryl trichloride, may be obtained by the direct addition of sulphur to the trichloride, exactly as the oxychloride is formed by the assimilation of oxygen (Henry). It may also be prepared by the action of sulphuretted hydrogen upon phosphorus pentachloride (Serullas)—



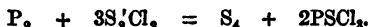
It may also be obtained by the action of the pentachloride upon antimony tersulphide (Baudimont)—



or by heating phosphorus pentasulphide together with the pentachloride (Thorpe)—



or by heating phosphorus with sulphur chloride, and distilling when the whole is dissolved (Chevrier)—



Phosphorus sulphochloride is a colourless, mobile liquid, of a pungent and slightly aromatic odour. Its sp. gr. is 1.63; it boils at 126° , and is but slowly decomposed by water, forming phosphoric and hydrochloric acids, together with sulphuretted hydrogen—

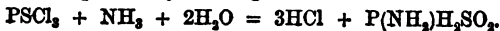


With caustic potash solution it yields *potassium sulphyphosphate*, or *potassium thiophosphate*—

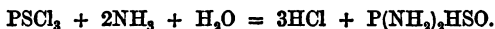


The acid is known only in combination; when liberated by an acid, it is quickly decomposed.

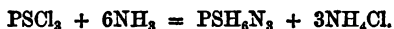
In contact with dilute ammonia the sulphochloride yields *thiophosphamic* or *sulphyphosphamic* acid. This compound may be regarded as thiophosphoric acid, in which an atom of hydroxyl is replaced by amidogen—



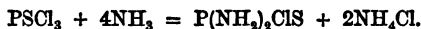
If the ammonia is concentrated, *thiophosphodiamic acid* is formed by the substitution of 2 atoms of NH_2 for 2 atoms of HO .



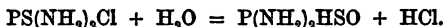
According to Schiff, phosphorus sulphochloride is converted by ammonia gas into *sulphophosphotriamide* and sal-ammoniac, thus—



According to Gladstone and Holmes, the following reaction ensues—



When treated with water the product yields thiophosphodiamic acid—



Phosphorus unites directly with bromine to form two compounds—the tribromide and the pentabromide; the combination is attended with the evolution of heat and light, and sometimes with explosion.

279. Phosphorus Tribromide, PBr_3 , is easily prepared by dissolving phosphorus and bromine, in the proper proportions, in separate portions of carbon bisulphide, mixing the liquids and distilling. The carbon bisulphide is readily separated from the trichloride by fractional distillation.

Phosphorus tribromide is a transparent mobile liquid, which fumes in the air, and readily volatilizes. In its chemical deportment it resembles the trichloride.

280. Phosphorus Pentabromide, PBr_5 , is formed by the action of an excess of bromine upon phosphorus. It is a yellow, solid substance, which fumes strongly in the air, crystallizes after fusion, and may be obtained in needle-shaped prisms by sublimation. It closely resembles the pentachloride in its behaviour with reagents.

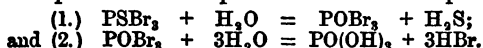
281. Phosphorus Bromochloride, PCl_2Br , may be formed by adding bromine to the trichloride. The two substances unite with the evolution of heat, and in a freezing mixture the compound crystallizes out. On melting it decomposes into two layers or solutions of the two bodies in one another; if, however, the mixture is kept solid for some days, it forms a homogeneous liquid on fusion. It is an orange-coloured

mass, which is resolved into phosphorus trichloride and bromine at 35°.

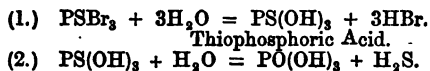
282. Phosphoryl Tribromide, POBr₃, may be obtained by exposing the pentabromide to a moist atmosphere, or by heating it with oxalic or boric acids. It is a solid crystalline substance, which melts at 45°, and boils at 195°.

283. Phosphoryl Chlorobromide, POCl₂Br, is a transparent, colourless liquid, of specific gravity 2.059, boiling at 136°, and solidifying, on being strongly cooled, to a crystalline mass, which melts at 11°. It turns yellow on exposure to light, and is decomposed by water with formation of phosphoric, hydrochloric, and hydrobromic acids.

284. Phosphorus Sulphobromide, PSBr₃, may be obtained by processes analogous to those which yield the sulphochloride. It crystallizes in yellow octahedrons of specific gravity 2.85, which melt at 38°. It has a penetrating, aromatic smell, and its vapour attacks the eyes. When once melted it remains liquid for days, but solidifies immediately on contact with a solid body. With water it yields sulphur, hydrogen sulphide, hydrobromic, phosphorous, and phosphoric acids. The following equations represent this decomposition. One portion is thus decomposed—



Whilst a second is converted into *thiophosphoric acid*, which immediately decomposes into hydrogen sulphide and phosphoric acid—



The sulphur and phosphorous acid are produced by the mutual action of the sulphuretted hydrogen and phosphoric acid.

285. Phosphorus Sulphobromochloride, PSCl₂Br, has also been obtained. It cannot be distilled unchanged, but as it is only slowly acted upon by water, it may be volatilized in a current of steam.

286. Pyrophosphoryl Sulphobromide, $\left. \begin{matrix} \text{P(Br)}_2\text{S} \\ \text{P(Br)}_2\text{S} \end{matrix} \right\} \text{S}$, is obtained by the action of bromine upon phosphorus tri-

sulphide, P_2S_3 . It is a yellow liquid of pungent odour, which fumes strongly in the air, and becomes turbid from separation of sulphur. Its sp. gr. is 2.262; it cannot be distilled without decomposition. When heated it is resolved into sulphur, phosphorus pentasulphide, and a yellow liquid having the composition $P_2SBr_6 = (PSBr_3 + PBr_3)$, which boils at 205° , and solidifies at -5° . On treatment with water, this substance is converted into a yellow crystalline substance of the composition $PSBr_3 + H_2O$ (Michaelis).

287. Metaphosphoryl Sulphobromide, PS_2Br , was obtained by Michaelis in preparing the preceding substance. It is insoluble in ether, by means of which it may be separated from the pyrophosphoryl compound. It forms a characteristic crystalline compound with alcohol of the composition $P_2S_3(OC_2H_5)_2(SC_2H_5)_2$, known as *diethoxyl-diethylsulphyl-pyrophosphoric ether*.

288. Phosphorus unites with iodine in two proportions to form the di-iodide, PI_2 (to which there is no corresponding chlorine or bromine compound), and the tri-iodide PI_3 . They are prepared by mixing solutions of phosphorus and iodine in carbon bisulphide. *Phosphorus Di-iodide* is deposited from its solution in carbon bisulphide in orange-coloured prisms, which melt to a red liquid at 110° . *Phosphorus Tri-iodide* crystallizes in dark red hexagonal plates, which melt at 55° , and are decomposed by water with formation of hydriodic and phosphorus acids.

No oxyiodide of phosphorus is known.

289. Phosphorus Fluoride, PF_3 , is a colourless, inflammable liquid obtained by distilling lead fluoride with phosphorus.

290. Phosphorus Cyanide, PCy_3 , is formed when silver cyanide is heated with phosphorus trichloride in a sealed tube. It forms long white needles, which take fire when touched with a heated rod. It melts at 203° , and distils unchanged at a few degrees above its melting point.

291. Phosphorus Sulphides and Selenides. — Phosphorus and sulphur readily unite when heated together. With ordinary phosphorus the reaction is accompanied with the evolution of light and heat, but with the amorphous variety the combination is far less rapid, although still at-

tended with a considerable rise of temperature. The following sulphides have been described:—

Phosphorus	Subsulphide,	P_2S
„	Monosulphide,	P_2S
„	Sesquisulphide,	P_2S_3
„	Trisulphide,	P_2S_3
„	Pentasulphide,	P_2S_5
„	Persulphide,	P_2S_{13}

They are prepared by heating the two substances together in the necessary proportions. The sub- and mono-sulphide are capable of existing in two distinct modifications, each forming a colourless liquid and a red solid. The remaining sulphides are yellow crystalline solids; they dissolve in caustic alkalies, and unite directly with many metallic sulphides to form compounds termed *sulphosphites* and *sulphosphates*.

Corresponding *phosphorus selenides* have been prepared by direct synthesis. The subselenide, P_2Se , is a dark yellow, fetid oil, which takes fire in contact with air, and is decomposed by water and caustic alkalies. The other selenides are red powders; phosphorus triselenide can scarcely be distinguished from amorphous phosphorus in outward appearance. These compounds are decomposed by caustic alkalies, and unite with metallic sulphides to form *seleniophosphites* and *seleniophosphates*.

292. Arsenic—Symbol As; atomic weight 75; vapour density 150.—This element, in combination with oxygen as arsenious oxide, and with sulphur as orpiment and realgar, has long been known. Arsenic is occasionally found native, generally in botryoidal or kidney-shaped masses, more rarely in rhombohedral crystals.

In small quantities arsenic is one of the most widely diffused of the elements; it is found accompanying many minerals; it is frequently present in iron pyrites and native sulphur, and hence finds its way into sulphuric acid. Many iron ores contain arsenic in small quantities, and it has been detected in certain ferruginous deposits from mineral waters.

The most abundant sources of the element are the arsenides of iron, $FeAs_2$ and Fe_2As_3 , and the double sulphide of

arsenic and iron, $\text{FeAs}_2 \cdot \text{FeS}_2$. When these substances are heated out of contact with air arsenic sublimes, and iron or ferrous sulphide remains behind. Arsenic is also obtained by heating the trioxide mixed with charcoal in earthen crucibles surmounted with iron caps. Arsenic, when freshly sublimed, has a bright metallic lustre, and white or steel gray colour. Its physical properties vary with the manner in which it is obtained. When condensed upon a hot surface it forms a compact, highly lustrous mass. In this form it is permanent in the air, and may be heated to 100° without suffering oxidation. As obtained by the reduction of arsenious oxide it forms a dark gray powder, or loosely aggregated mass, which readily oxidizes even at ordinary temperatures. Arsenic crystallizes in rhombohedrons, isomorphous with antimony and tellurium. They are exceedingly brittle, and may easily be reduced to powder. Arsenic is capable of existing in several allotropic modifications, which are mainly distinguished by differences in specific gravity. When sublimed in an atmosphere of hydrogen or deposited by the decomposition of the hydride (*vide infra*), it is partially converted into an amorphous, black, vitreous mass of sp. gr. 4.71. In this form it maintains its lustre unimpaired for a considerable time on exposure to the air, and is but slowly acted upon by dilute nitric acid. When heated to 360° it is transformed into the crystalline modification with evolution of heat; in this state arsenic has the sp. gr. 5.727 (Bettendorf). These varieties of arsenic are analogous to the crystalline and amorphous forms of red phosphorus.

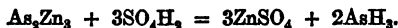
Heated in a vacuum tube or under the ordinary pressure of the atmosphere, arsenic sublimes without previous fusion. It may be fused, however, by heating it under pressure. Arsenic vapour has an exceedingly oppressive odour of garlic. Its vapour density is anomalous, being double its atomic weight. Its molecule, like that of phosphorus, occupies in the gaseous state only half the volume of the hydrogen molecule.

COMBINATIONS OF ARSENIC AND HYDROGEN.

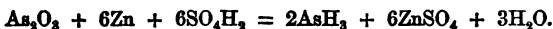
Arsenic combines with hydrogen in at least two proportions to form a gaseous and a solid compound. The former has the

composition AsH_3 ; the latter that of AsH_2 , or possibly, As_2H_4 .

293. Arsenic Trihydride, or Arseniuretted Hydrogen, AsH_3 , was discovered by Scheele in 1755, and may readily be obtained by dissolving zinc or potassium arsenide in dilute sulphuric acid—

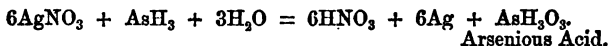


Or, more simply, by dissolving zinc in dilute sulphuric acid containing the tri- or pent-oxide of arsenic—

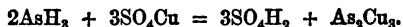


These processes yield the gas mixed with free hydrogen.

Arseniuretted hydrogen is a colourless gas, of repulsive odour. It is highly poisonous; even when largely diluted with air it produces nausea and headache. It liquefies at -30° ; it has not yet been solidified. It is but slightly soluble in water. A current of the gas passed into a solution of silver nitrate precipitates the silver in accordance with the following reaction—



From a solution of copper it throws down copper arsenide—



The gas burns in the air with a lavender-coloured flame, forming water and arsenic trioxide, which volatilizes, and may be condensed upon a cold surface, such as the lid of a porcelain crucible held above the flame. If the lid be pushed down into the flame, metallic arsenic is deposited. The decomposition of the arseniuretted hydrogen is also effected by passing it through a tube heated to redness. These reactions are frequently employed in the detection of arsenic (see "Detection of Arsenic").

The solid hydride of arsenic is produced in the electrolytic decomposition of water when the negative pole is formed of arsenic. It is also obtained by the action of water on potassium or sodium arsenide. It is a brown powder, which burns, when heated in the air, with a yellow light; when heated to 200° in closed vessels it evolves its hydrogen.

The same compound appears to be formed when zinc arsenide is dissolved in dilute hydrochloric acid. According to Soubeiran, it has the composition AsH_2 ; from the more recent observations of Wiederhold, its formula would appear to be As_4H_2 .

COMBINATIONS OF ARSENIC AND OXYGEN.

Arsenic forms two oxides, viz., the trioxide, As_2O_3 , and the pentoxide, As_2O_5 . The former compound is formed when the metal burns in the air or in oxygen; the latter oxide, or rather the corresponding acid, is produced by the action of energetic oxidizing reagents, *e. g.*, nitric or permanganic acids, upon the metal or the trioxide. When arsenic acid is heated it is converted into the pentoxide by loss of water.

294. Arsenic Trioxide, or *Arsenious Oxide*, As_2O_3 , has been known from very early times. It constitutes the mineral known as *arsenite*, and is formed artificially on the large scale by roasting arsenical ores in a current of air. The vaporized arsenious oxide is led through a series of condensing chambers, where it is deposited in fine powder. By resublimation it is obtained as a glassy mass, constituting the vitreous or amorphous form of arsenic trioxide. When freshly prepared this variety is perfectly transparent, but in time it becomes opaque by passing into the crystalline modification. Amorphous arsenious oxide has the specific gravity 3.738. Arsenious oxide may be obtained crystallized in two distinct forms, viz., in octahedrons and in rhombs. The *octahedral form* is produced when the vapour of the trioxide condenses upon a cold surface, or when a saturated solution in hot water or hydrochloric acid is allowed to cool. This form of the oxide has a specific gravity of 2.695. The *rhombic variety* is isomorphous with *valentinite* or native antimony trioxide. It is found native in colourless, semi-transparent, flexible crystals of specific gravity 3.85, and is deposited from an alkaline solution of the oxide. This would appear to be the more unstable form of arsenious oxide, since on heating, or by solution in hot water, it is converted into the octahedral variety.

When heated to 220° the crystalline modifications are con-

verted, without previous fusion, into a colourless, inodorous vapour, which is nearly 14 times heavier than air; by heating the oxides under pressure they may be fused before they volatilize. The vitreous form of the oxide may be fused under the ordinary pressure.

Arsenic trioxide is but slightly soluble in cold water; a saturated solution contains only about 2 per cent. The oxide dissolves more readily and to a greater extent in hot water. The amorphous arsenious oxide appears to be slightly more soluble in water than the crystalline variety; but the solution of the vitreous modification is retarded by the difficulty of bringing the water into intimate contact with the oxide. When a small quantity of the finely powdered oxide is thrown into water, the greater portion swims upon the surface, and it is only after protracted boiling that the particles become thoroughly wetted. Hot dilute mineral acids dissolve the oxide to a greater extent than water, but the greater portion is deposited as the solution cools.

A solution of arsenic trioxide in water (arsenious acid) has very feeble acid properties. The oxide dissolves in potash or soda solutions, but without destroying the alkaline reaction of these substances. On exposure to air, the solution gradually absorbs carbon dioxide, and the arsenious oxide is deposited in crystals, which, from the slowness of their formation, frequently acquire a considerable size. Sodium arsenite is used by the calico printer. The greater number of the arsenites are insoluble in water. The most important are the copper and silver salts. Copper arsenite, or Scheele's green (CuHAsO_3 ?), is employed as a pigment. It may be formed by adding a salt of copper to a solution of potassium arsenite. A copper aceto-arsenite, $3\text{CuAs}_2\text{O}_7(\text{C}_2\text{H}_3\text{O}_2)_2\text{Cu}$, known as Schweinfurth, or imperial green, is also largely used as a pigment. It is prepared by mixing arsenious oxide with copper acetate and water. Silver arsenite, Ag_3AsO_3 , is obtained as a light yellow precipitate on adding a solution of silver nitrate to an alkaline arsenite. It gradually changes colour on exposure to light, and is decomposed when heated. It readily dissolves in acetic acid, and is thus distinguished from silver orthophosphate. Its formation is frequently used as a test for arsenious oxide.

Arsenious oxide is highly poisonous, a dose of two or three grains being sufficient to cause death. Despite its intense toxical action, it is consumed by the Tyrolese mountaineers with the alleged object of improving the power of their respiratory organs. By gradually accustoming themselves to its action, the peasants are capable of taking doses which to most persons would be attended with fatal consequences.

295. Arsenic Pentoxide, As_2O_5 .—Arsenious oxide, heated with nitric acid, or suspended in water and treated with chlorine, is converted into arsenic acid, H_3AsO_4 . When a concentrated solution of the acid is allowed to stand, it deposits transparent, deliquescent prisms of the composition $2\text{H}_3\text{AsO}_4 + \text{H}_2\text{O}$. These when heated to 100° melt, and give up their water of crystallization.

296. Pyroarsenic Acid, $\text{H}_4\text{As}_2\text{O}_7$, is formed by heating the crystallized acid to 160° . When redissolved in water it appears to be transformed into the ordinary acid.

297. Meta-arsenic Acid, HAsO_3 , is obtained by heating the pyro acid to 200° . It is a white, nacreous powder, which on treatment with water dissolves with the evolution of great heat, and is converted into the ordinary acid.

At a still higher temperature the acid parts with the whole of its water, and is transformed into arsenic pentoxide. This substance may remain in contact with water for some hours without much change, but after a time it suddenly assimilates the water, and rapidly dissolves with the production of heat. At a red heat it is resolved into arsenious oxide and free oxygen.

Arsenic acid is now manufactured on a large scale for the use of the dyer and calico printer. It is also employed to a considerable extent in the manufacture of the so-called coal-tar colours.

Arsenic acid is poisonous, although not to the same extent as the trioxide. A strong solution of the acid acts rapidly upon the skin, producing painful blisters.

Arsenic acid is tribasic, and many of its salts are isomorphous with the corresponding phosphates. The most important arsenates are the disodium salt, Na_2HAsO_4 , which is used to a large extent as a mordant; ammonium-magnesium

arsenate, $\text{Mg}(\text{NH}_4)\text{AsO}_4$, a highly insoluble compound, which on heating is resolved into magnesium pyroarsenate, $\text{Mg}_2\text{As}_2\text{O}_7$; and silver arsenate, Ag_3AsO_4 , a reddish-brown precipitate formed by adding silver nitrate to sodium arsenate. It is readily soluble in ammonia, and in acetic and nitric acids. Many arsenates occur native—*e.g.*, *haidingerite*, $2\text{CaHAsO}_4 + \text{H}_2\text{O}$; *pharmacolite*, $\text{CaHAsO}_4 + 5\text{H}_2\text{O}$; *olivinite*, $\text{Cu}_3(\text{AsO}_4)_2\text{CaH}_2\text{O}_2$; *nickel bloom*, $\text{Ni}_2(\text{AsO}_4)_2$. These minerals have been obtained artificially in crystals by heating the corresponding metallic carbonates with an aqueous solution of arsenic acid in sealed tubes.

COMBINATIONS OF ARSENIC WITH THE HALOGENS.

Arsenic readily combines with the halogens. When finely powdered it takes fire in an atmosphere of chlorine or bromine.

298. Arsenic Trichloride, AsCl_3 , is formed by the direct union of its components, or by heating a mixture of arsenic and mercuric chloride, or by distilling arsenious oxide with strong hydrochloric acid, or with a mixture of salt and sulphuric acid, or by passing chlorine over heated arsenic trioxide. It forms a colourless, oily liquid, which boils at 132° , and remains liquid at -29° . In contact with a small quantity of water it is converted into an oxychloride of the composition AsClO or $\text{AsCl}_2 \cdot \text{As}_2\text{O}_3$. It is a viscid, semi-transparent, fuming mass, which when strongly heated is converted into a vitreous substance of the composition $\text{AsClO} \cdot \text{As}_2\text{O}_3$. With excess of water arsenic trichloride is decomposed into arsenious and hydrochloric acids. Arsenic trichloride unites directly with ammonia to form an ammonio-arsenic chloride of the composition $2\text{AsCl}_3 \cdot 7\text{NH}_3$, which is soluble in water, and alcohol without decomposition. On boiling the aqueous solution the compound is decomposed into arsenious acid and sal-ammoniac.

299. Arsenic Tribromide, AsBr_3 , may be obtained in a similar manner to the trichloride, or more readily by agitating powdered arsenic with bromine dissolved in carbon disulphide. It crystallizes in deliquescent prisms of sp. gr. 3.66,

melts at about 20° , and may be volatilized unchanged. Several oxybromides of arsenic have been prepared.

No pentabromide or chloride of arsenic has been obtained.

300. Arsenic Tri-iodide, AsI_3 , is formed by the direct union of its elements. It is an orange-coloured crystalline substance, soluble in water (by which it is slowly decomposed) and in alcohol, from which it may be obtained crystallized in bright red, shining plates. In contact with boiling water it is gradually converted into an oxyiodide of the composition, $\text{As}_2\text{I}_2\text{O}_{11} = 2\text{AsIO} \cdot 3\text{As}_2\text{O}_3$.

301. Arsenic Trifluoride, AsF_3 , is obtained by distilling fluorspar and arsenic trioxide with sulphuric acid. It is a fuming, highly volatile liquid of sp. gr. 2.73, it boils at 63° , and is decomposed by water, forming arsenious and hydrofluoric acids.

302. Arsenic Pentafluoride, AsF_5 , is known only in combination with certain metallic chlorides. The following compounds have been obtained by Marignac:—

Potassium Arsenic Fluoride, $2(\text{KF} \cdot \text{AsF}_5) \cdot \text{H}_2\text{O}$.
Dipotassium Arsenic Fluoride, $2\text{KF} \cdot \text{AsF}_5 \cdot \text{H}_2\text{O}$.

By repeated treatment with water, the former compound yields *potassium arsenic oxyfluoride*, $\text{KF} \cdot \text{AsOF}_2 + \text{H}_2\text{O}$.

COMBINATIONS OF ARSENIC WITH SULPHUR.

Arsenic combines with sulphur in at least three proportions to form sulphides of the composition As_2S_3 , As_2S_5 , and As_2S_7 .

303. Arsenic Disulphide, As_2S_3 , occurs in nature, constituting the mineral known as realgar or ruby sulphur. It may be obtained artificially by fusing arsenic and sulphur together in the proper proportions. It is used to some extent as a pigment, and in pyrotechny. *Indian white fire* consists of 24 parts nitre, 7 parts sulphur, and 2 parts realgar.

304. Arsenic Trisulphide, As_2S_3 , also occurs native, forming orpiment—the *auripigmentum* of the Romans. It is a bright yellow, crystalline body, of sp. gr. 3.4. It may be prepared artificially by passing a stream of sulphuretted hydrogen through a solution of arsenious oxide. It is pre-

pared on the large scale for use as a pigment, under the name of king's yellow, by subliming a mixture of arsenic oxide and sulphur. Arsenic trisulphide is readily dissolved by solutions of the alkaline carbonates and oxides, and unites directly with many metallic sulphides, forming salts termed *sulpharsenites*. The ammonium compound, formed by dissolving arsenic trisulphide in ammonium sulphide solution, has the composition $2(\text{NH}_4)_2\text{S} \cdot \text{As}_2\text{S}_3$.

305. Arsenic Pentasulphide, As_2S_5 , cannot be obtained by precipitating a solution of arsenic acid by sulphuretted hydrogen. The precipitate so formed is a mixture of the trisulphide and free sulphur, in the proportion required by the formula, As_2S_5 .

The pentasulphide is known, however, in combination with metallic sulphides, forming the so-called *sulpharsenates*. The general formulæ of these salts are—

Metasulpharsenate,.....	MAsS_3
Pyrosulpharsenate,	$\text{M}_2\text{As}_2\text{S}_7$
Orthosulpharsenate,.....	M_3AsS_4

analogous to the meta, pyro, and ortho modifications of phosphoric acid.

306. Detection of Arsenic.—Arsenic compounds, more especially arsenious oxide, are occasionally made use of for criminal purposes; few poisons, however, are more readily detected than arsenic. Arsenious oxide itself may be distinguished by giving, with ammoniacal silver nitrate solution, a yellow precipitate of silver arsenite; and, with ammoniacal cupric sulphate, a light green precipitate of copper arsenite (Scheele's green). An aqueous solution of arsenious acid, acidulated with hydrochloric acid, gives a yellow precipitate of arsenic sulphide when treated with sulphuretted hydrogen. If the arsenic sulphide be collected, dried, mixed with potassium cyanide, and heated in a narrow tube, a black ring of reduced arsenic will be obtained. If the portion of the tube containing the sublimate is cut off by means of a file, and introduced into a wider tube and heated, the arsenic combines with oxygen, and is converted into arsenious oxide, which condenses in shining microscopic octohedra, on the colder portions of the wider tube. The fragment of the narrow tube may be thrown out, and the sub-

limate of arsenious oxide dissolved in a few drops of hot water, and treated with silver nitrate and copper sulphate solutions, as above described.

The ease with which a solution of arsenious acid gives rise to arseniuretted hydrogen, in presence of nascent hydrogen, may be applied to the detection of arsenic. If the solution containing the arsenic be poured into a flask in which hydrogen is being generated from zinc and sulphuric acid, arseniuretted hydrogen will be formed. The flame of the issuing hydrogen will be coloured characteristically grayish-violet, and white fumes of arsenious oxide will be formed. If a piece of paper moistened with ammonia-nitrate of silver be held over the flame, it will quickly be stained yellow from the

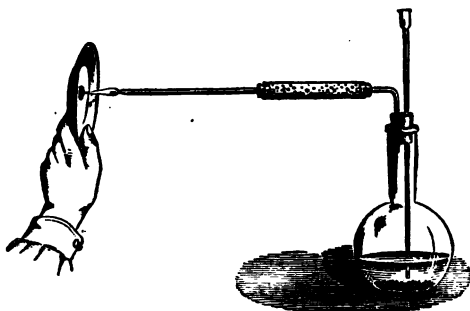


Fig. 112.

formation of silver arsenite. If a piece of porcelain be thrust into the middle of the flame, brownish-black lustrous stains of arsenic will be deposited on the porcelain (fig. 112). On heating the glass jet through which the gas passes to low redness, the arseniuretted hydrogen will be decomposed, and a highly lustrous mirror of arsenic will be formed within the tube. The portion of tube containing the mirror may be cut off and oxidized in a wider tube; on dissolving the sublimed arsenious oxide in water, its solution will give the characteristic precipitates with copper and silver salts.

If a strip of bright copper foil be boiled with a solution of arsenious oxide, arsenic will be quickly deposited on the foil, which thereby loses its characteristic reddish colour, and

becomes gray. If the strip be dried by filter paper, and heated in a wide tube, the arsenic is oxidized and sublimes. The solution of the sublimate in water must be tested with copper and silver salts. This method of detecting arsenic is known as "Reinsch's test."

It occasionally happens that arsenic has to be sought for in highly complex mixtures, containing large quantities of organic matter, as in soup, gruel, the liquid contents of the stomach, &c. The presence of the organic matter interferes with the direct application of the above tests. The organic matter may readily be destroyed by heating the liquid with hydrochloric acid and potassium chlorate. After the complete expulsion of the excess of chlorine the liquid is to be treated with sulphuretted hydrogen, which gradually reduces the arsenic acid formed by the oxidizing action of the chlorine to the state of arsenious acid, and afterwards converts it into arsenic tri-sulphide. The impure arsenic sulphide thus formed is collected, dried, and heated with a drop or two of sulphuric acid to char organic matter, redissolved in water, filtered, and again precipitated by sulphuretted hydrogen. The sulphide may then be reduced by potassium cyanide, as described above.

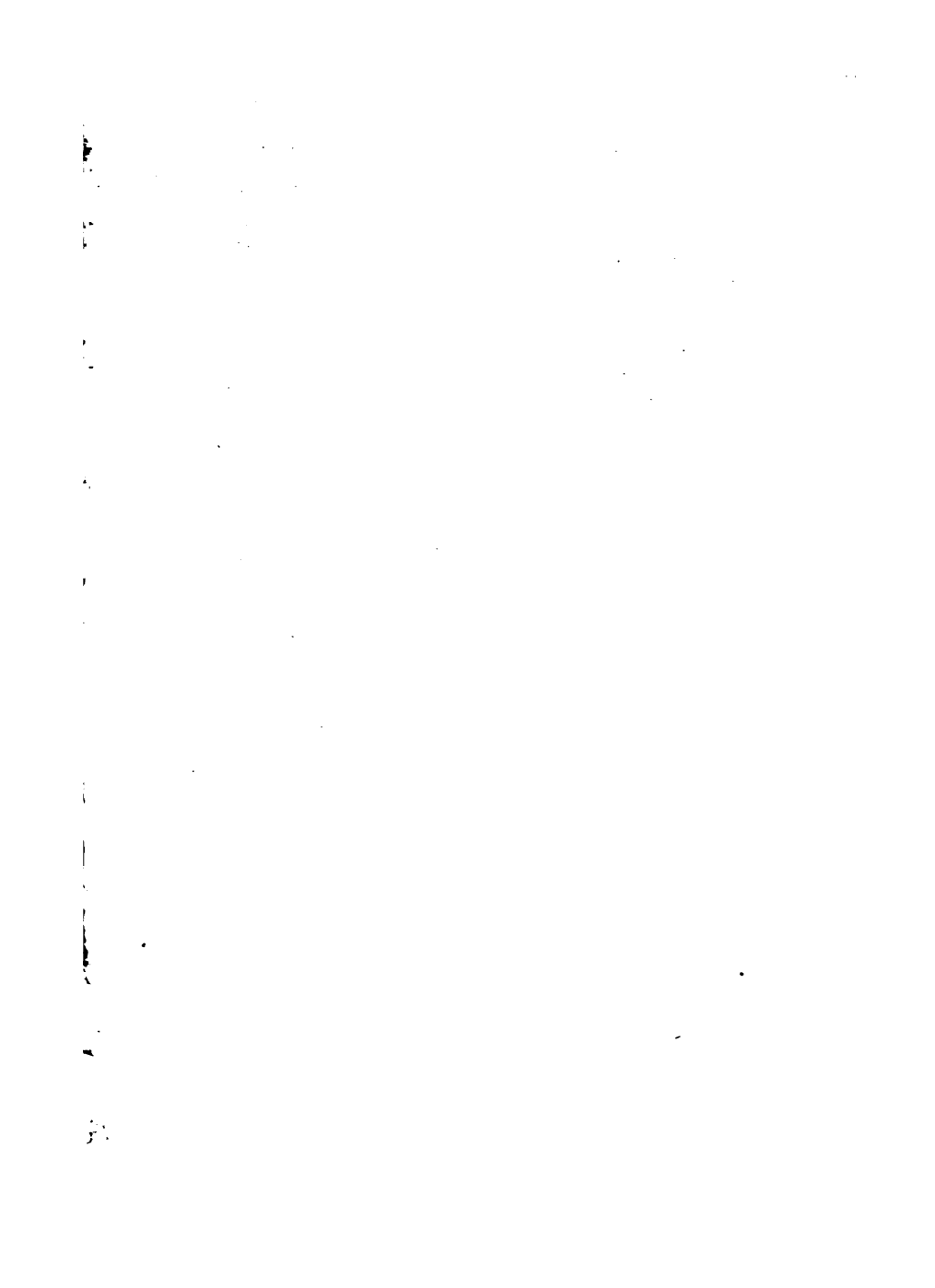
Or instead of the foregoing method, the solution may be boiled with pure dilute sulphuric acid for a short time, whereby the starch is converted into dextine, and albuminous substances, casein, &c., are coagulated. The liquid is filtered, treated with sulphuretted hydrogen, the impure sulphide heated with pure *aqua regia* to destroy organic matter, the liquid is evaporated to dryness, and the residue dissolved in dilute hydrochloric acid, reduced with sulphur dioxide, boiled, and again treated with sulphuretted hydrogen. The sulphide now obtained may be dried and heated with potassium cyanide, or with a mixture of powdered charcoal and sodium carbonate.

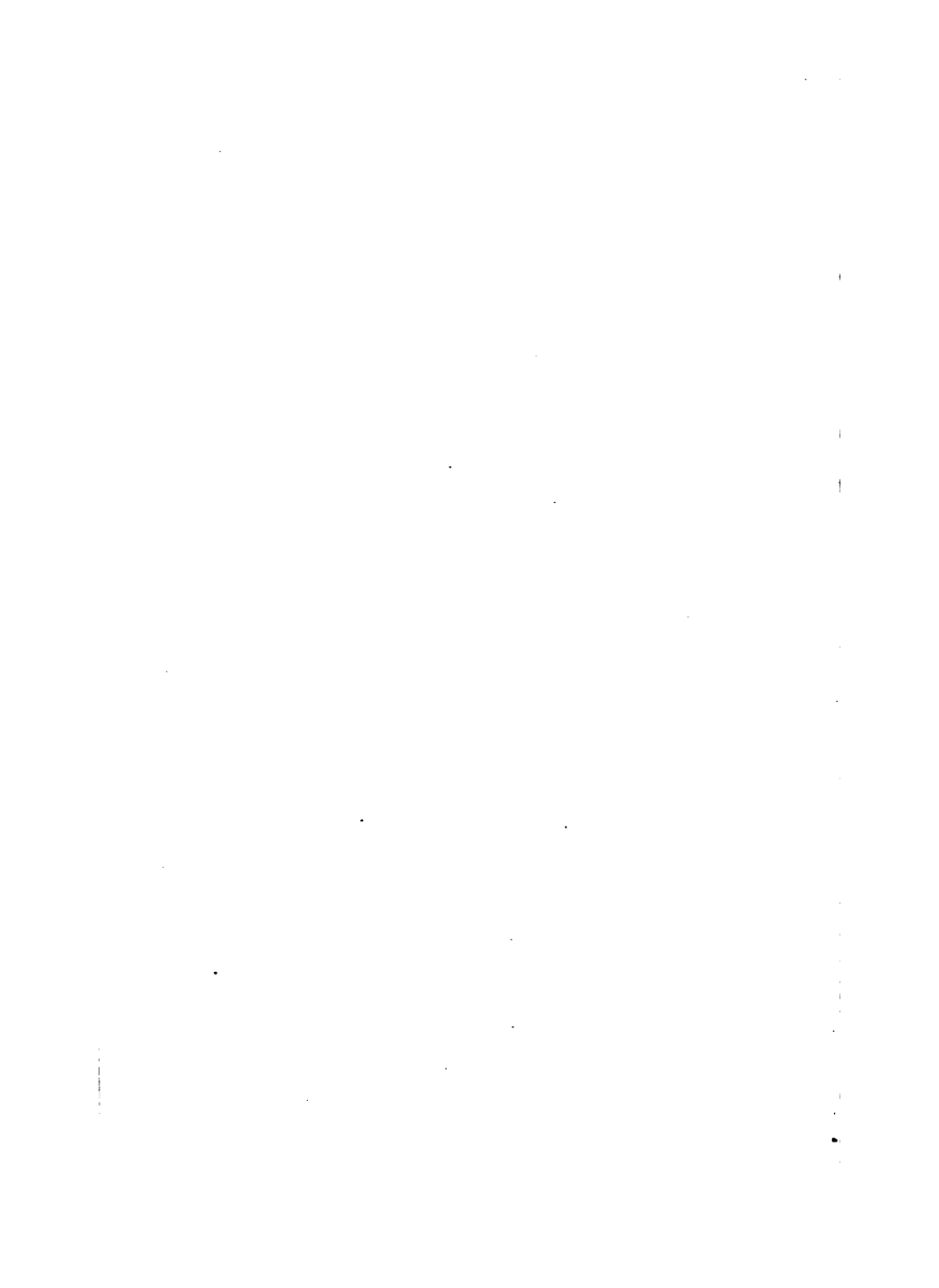
On account of its sparing solubility, it may happen that a portion of the arsenious oxide contained in the liquid to be examined may be undissolved, and a careful search in the lining of the stomach or in the sediment formed in the organic liquid may reveal it in the form of small, gritty, white particles. If these are found, they should be collected and

dried with bibulous paper, and heated in a narrow tube with a fragment of charcoal previously heated to redness. The vaporized arsenious oxide in contact with the charcoal is reduced, and the arsenic condenses upon the tube. The mirror thus obtained is oxidized in a wider tube, and the arsenious oxide formed is dissolved in water and tested with silver nitrate and copper sulphate solutions. As arsenious acid in solution readily passes through a moistened membrane, whereas the greater portion of the organic matter contained in the liquid of the stomach, or in gruel, soup, &c., is incapable of so passing, Graham has proposed to separate the arsenic by dialysis. The organic liquid is poured upon the dialyser, which is floated in a basin containing pure water. In a few hours the arsenious oxide, together with any other crystallized substance which may be present, passes into the pure water, and the solution, after concentration, may be treated with sulphuretted hydrogen, and the identity of the sulphide confirmed by the tests above given.

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